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Preliminary Concepts: Coordinated Safeguards for Materials Management in a Thorium-Uranium Fuel Reprocessing Plant

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EXECUTIVE SUMMARY

This report describes the preliminary safeguards concepts necessary for nuclear-materials management in a thorium-uranium fuel reprocessing plant. The thorium reprocessing plant is the fifth in a series of nuclear facilities for which conceptual designs of advanced nuclear-materials management systems have been provided by the Safeguards Systems Group (Q-4) of the Los Alamos Scientific Laboratory (LASL), under the direction of the US Department of Energy's Office of Safeguards and Security (DOE-OSS). These conceptual design studies are part of a continuing effort to develop improved safeguards systems for a broad spectrum of nuclear fuel-cycle facilities. Previous reports include safeguards systems for nuclear-materials management in mixed-oxide fuel fabrication facilities (LA-6536), plutonium fuel reprocessing plants (LA-6881), plutonium nitrate conversion plants (LA-7011), and fast critical facilities (LA-7315).

This report and a companion study, "A Critical Review of Analytical Techniques for Safeguarding the Thorium-Uranium Fuel Cycle" (LA-7372), were prepared at the request of DOE's Nuclear Production Division, in support of the Savannah River Laboratory's Alternative Fuel Cycle Technology (AFCT) Program. Subsequent studies for the AFCT will extend and quantify the findings of this preliminary analysis and will include safeguards conceptual designs for facilities in which uranium and plutonium are coprocessed.

This report addresses preliminary concepts for coordinated safeguards materials management in a generic chemical separations facility involved in reprocessing uranium-thorium fuels, using a uranium-thorium-fueled light-water reactor (LWR) fuel reprocessing plant as a reference facility. The process flow sheets for the reference facility were modified from conventional Purex, Thorex, and HTGR reprocessing technology by the LASL Safeguards staff and may differ in detail from those finally adopted by the AFCT. The report is preliminary in the sense that the concepts

developed herein will be transferred eventually to the process actually selected and quantified subsequently by modeling and simulating the safeguards system and the final version of the process and facility as a unit. As was done for the facilities previously studied, the results of this activity will be reported as an LA-series report that will supersede this LAMS-series report.

Originally, reactor designs for the uranium-thorium fuel cycle relied on initial core loadings of high-enriched uranium-235 (^{235}U). Subsequent recycle cores were to contain high-enriched uranium-233 (^{233}U), produced from the thorium during operation of the initial core, or mixtures of ^{235}U and ^{233}U. Because both these uranium isotopes are usable in nuclear weapons, nonproliferation considerations have invoked the concept of denaturing these materials by diluting them with nonfissile uranium-238 (^{238}U) to concentrations where they are no longer useful for weapons (12% for ^{233}U and 20% for ^{235}U). The secondary consequences of this dilution are a loss in economic and neutronic efficiency and the production of significant quantities of weapons-usable plutonium, which is not normally produced in high-enriched uranium-thorium reactor systems. The plutonium-239 (^{239}Pu), formed by parasitic neutron capture in the ^{238}U present in denatured uranium-thorium reactors, is about one-third of that produced in a LWR operated on the plutonium-uranium cycle.

The reference facility is designed to process first-generation uranium-thorium (denatured ^{235}U) startup fuels as well as first-recycle and equilibrium (denatured ^{233}U) uranium-thorium LWR fuels, and to recover the plutonium generated in the ^{238}U denaturant. Fissile fuel content is limited to less than 20% ^{235}U and to less than 12% ^{233}U in the denatured fuels.

Although several alternative modes of operation are discussed, safeguarding the reference facility is complicated by the necessity to maintain four component streams separately: co-recovery of ^{235}U from initial core loadings and ^{233}U

generated from thorium; thorium; plutonium; and fission products and other wastes. Thus, the facility combines features from two chemical separations plants, one based on the Purex process, the other on the Thorex process.

Because no facility of this nature has ever been demonstrated, both the reference facility and its safeguards system must rely heavily on information extrapolated from extensive experience with plutonium-uranium reprocessing facilities, and to a lesser extent on information obtained from high-temperature gas-cooled reactor (HTGR) studies. The process and safeguards analogies for the uranium-thorium cycle are weakest in the areas of dissolving the refractory thorium oxide fuels, disposing of the plutonium produced in the denatured fuels, and resolving problems associated with the greater induced radioactivity in thorium recycle fuels.

Gross radiation effects arising from the presence of ^{232}U daughters and other secondary products of the denatured uranium-thorium fuel cycle may be more readily addressed by process and operations changes than at the safeguards and materials-measurement level. Accurate materials measurement in the presence of these gross radiation fields and the spectral radiation from the entire suite of uranium isotopes plus plutonium, thorium, protactinium, and their daughters has yet to be demonstrated under realistic operational conditions.

It is undoubtedly true that this hostile radiation environment will tend to desensitize most measurement techniques below the levels obtained with the relatively simple isotopic mixes characteristic of conventional fuel reprocessing plants. The quantitative extent of these effects will be addressed in a subsequent report; however, this report discusses their general influence, suggests means for improving this situation, and identifies areas requiring further development and treatment in the projected detailed study and the subsequent final report.

Chapter I of this report briefly reviews the technical basis for the thorium-uranium fuel cycle. Some of the reactor concepts requiring aqueous reprocessing, and the aqueous

reprocessing philosophy, are summarized in Chapter II. A preliminary flowsheet for reprocessing denatured thorium-uranium fuels to produce separate thorium, uranium, and plutonium product streams is presented in Chapter III. A preliminary safeguards system for this plant is proposed in Chapter IV, and the measurement methodology required for the safeguards system is reviewed in Chapter V. The conclusions of this preliminary study are summarized in Chapter VI.

For the final report a plant design to be selected by SRL will be computer-modeled as the reference facility and operational parameters will be simulated. Accountability measurement techniques and the statistical sampling plans will be applied to the simulated SNM inventories. Alternative accounting and diversion strategies will be evaluated and compared using decision analysis tools adapted for this purpose. Recommendations for the most effective safeguards system will be made on the basis of these comparisons.

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by

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ABSTRACT

This report addresses preliminary concepts for coordinated safeguards materials management in a typical generic thorium-uranium-fueled light-water reactor (LWR) fuels reprocessing plant. The reference facility is designed to recover thorium and uranium from first-generation (denatured ^{235}U) startup fuels, first-recycle and equilibrium (denatured ^{233}U) thorium-uranium LWR fuels, and to recover the plutonium generated in the ^{238}U denaturant as well.

In a subsequent report a specific reference plant design selected under the Alternative Fuel Cycles Technology Program will be modeled and operational parameters will be simulated using the concepts developed here. Recommendations for the most effective safeguards system will be made on the basis of these comparisons.

I. INTRODUCTION

Thorium-based reactors have been proposed to extend world energy reserves, and more recently, as a means for improving the proliferation resistance of the nuclear fuel cycle. Thorium is not fissile and unlike uranium, it is of no value as a primary nuclear fuel. However, in an operating nuclear reactor ^{232}Th

is converted to ^{233}U which, like ^{235}U and ^{239}Pu, can be used to produce useful energy. Uranium-233 also can be used in nuclear weapons and therefore must be safeguarded.

Thorium-based fuels can be substituted for uranium-based fuels in most reactor systems, with some tradeoffs in such areas as reactor behavior and fuel-cycle economics. It is not the purpose of this study to review or assess the physics and economics of the various reactor systems except to the extent that fuel and cladding types and fuel-utilization philosophy are important in designing fuel reprocessing facilities and, hence, for designing integrated safeguards materials control and accountability systems for these facilities.

Conventional light-water reactors (LWRs), heavy-water reactors (HWRs), and liquid-metal fast-breeder reactors (LMFBRs) have been studied extensively, and reactors using uranium and plutonium as fuels have been or are being commercialized. These systems are fueled with ^{235}U and/or ^{239}Pu, with ^{238}U serving as the fertile material. Regardless of whether or not the fuel is reprocessed, some of the plutonium formed in these reactors is consumed as fuel. In most of these conventional reactor systems thorium can be substituted for ^{238}U as the fertile material. In addition, thorium is used in high-temperature, graphite-moderated, gas-cooled reactors (HTGRs) and light-water thermal-breeder reactors (LWBRs).

The ^{233}U that is produced in thorium-based reactors can be used to fuel succeeding generation reactors; however, because ^{233}U does not occur in nature, the reactor must be loaded initially with either ^{235}U-enriched uranium or plutonium. Until now, most reactor concepts have relied on using high-enriched (93%) ^{235}U for the initial loading and essentially pure (reactor-grade) ^{233}U for second-generation reactors. This approach is driven largely by overall fuel-cycle economics and neutronic efficiency. Present United States nonproliferation policies dictate that uranium containing more than 20% ^{235}U or 12% ^{233}U cannot be used as commercial reactor fuel because at these higher enrichments the materials theoretically are usable

in weapons. Future reactor designs therefore must be based on diluting the fissile isotopes of uranium with ^{238}U (denaturing).

Irradiation of the denatured fuel in fast or thermal reactors leads to the production of ^{239}Pu by neutron capture in the ^{238}U diluent. Plutonium production is not considered to be a safeguards problem in highly enriched uranium fuel cycles, which produce only small amounts of plutonium, primarily ^{238}Pu formed by a series of neutron-capture reactions from ^{235}U. The ^{238}Pu, although highly toxic because of its high specific activity, is not useful as a weapons material. Plutonium produced from ^{238}U, however, consists largely of ^{239}Pu with lesser amounts of ^{240}Pu, ^{241}Pu, and ^{242}Pu, and is weapons usable. A significant feature on the denatured fuel cycle is that weapons-grade uranium is essentially eliminated, but at the expense of producing weapons-grade plutonium. The plutonium produced in the denatured fuel cycle is of the order of 20-35% of that produced in conventional LWRs and therefore requires nearly the same stringent safeguards measures.

Conventional LWR fuel initially enriched to 3% ^{235}U contains 1% ^{235}U and 1% plutonium at discharge. Reprocessing of this fuel recovers this fissile inventory but is not necessary for the short-term continuance of the LWR fuel cycle. Although the once-through or stowaway fuel cycle is being proposed as an alternative to reprocessing conventional LWR fuels, it will be necessary to reprocess these fuels to obtain fissile fuel for starting up any uranium-fueled breeder reactor such as the LMFBR.

The once-through fuel cycle is not a rational alternative to reprocessing in the thorium fuel cycle. The "raison d'être" for the thorium fuel cycle is to generate ^{233}U fuel for successive reactors, though some of the ^{233}U is burned in situ in the first generation reactor. Reprocessing of thorium fuels, therefore, is necessary for continuance of the thorium cycle because a large fraction of the fuel value otherwise would be discarded.

Thorium reprocessing technology will depend on the reactor design and fuel utilization philosophy. The reprocessing alternatives can range from recovering only ^{233}U to recovering

thorium, ^{233}U, ^{235}U, and plutonium in separate streams or coprocessing any combinations of these streams. This report will address primarily the technology for the aqueous reprocessing of separate streams as proposed in the Alternate Fuel Cycle Technologies (AFCT) Program being administered by the Savannah River Laboratory (SRL).[1,2]

II. URANIUM-THORIUM FUEL CYCLE CONCEPTS

As noted in the previous section, a number of concepts have been devised to extend energy resources by substituting thorium for uranium in fission reactors. The main purpose of thorium substitution is the production of fissile ^{233}U in place of ^{239}Pu. A portion of the ^{233}U is burned in situ; the remainder is reprocessed to fuel succeeding reactors.

The production chain for formation of uranium from thorium is shown in Fig. 1.[3] The main product is ^{233}U through the ^{233}Th-^{233}Pa chain, but other uranium isotopes are also produced. Formation of ^{235}U is beneficial in that it is fissile. However, ^{235}U has an appreciable neutron-absorption cross section for forming ^{236}U, which is a parasitic absorber and reduces the number of neutrons available for continuing the fission and conversion processes. Thus, in the overall neutron economy, ^{236}U is a poison, and fuel containing a significant concentration of ^{236}U must eventually be discarded.

An important side effect in the production of ^{233}U is the formation of low concentrations of ^{232}U resulting from successive neutron absorption by ^{230}Th or by an (n,2n) reaction from ^{232}Th, ^{233}Pa, or ^{233}U. The formation and decay of ^{232}U is summarized in Fig. 2 (Ref. 4). For either of the (n,2n) reactions a neutron energy >6 MeV is required, and formation of ^{232}U through these reactions is not significant in well-thermalized reactors. The ^{230}Th thus becomes the main source of ^{232}U.

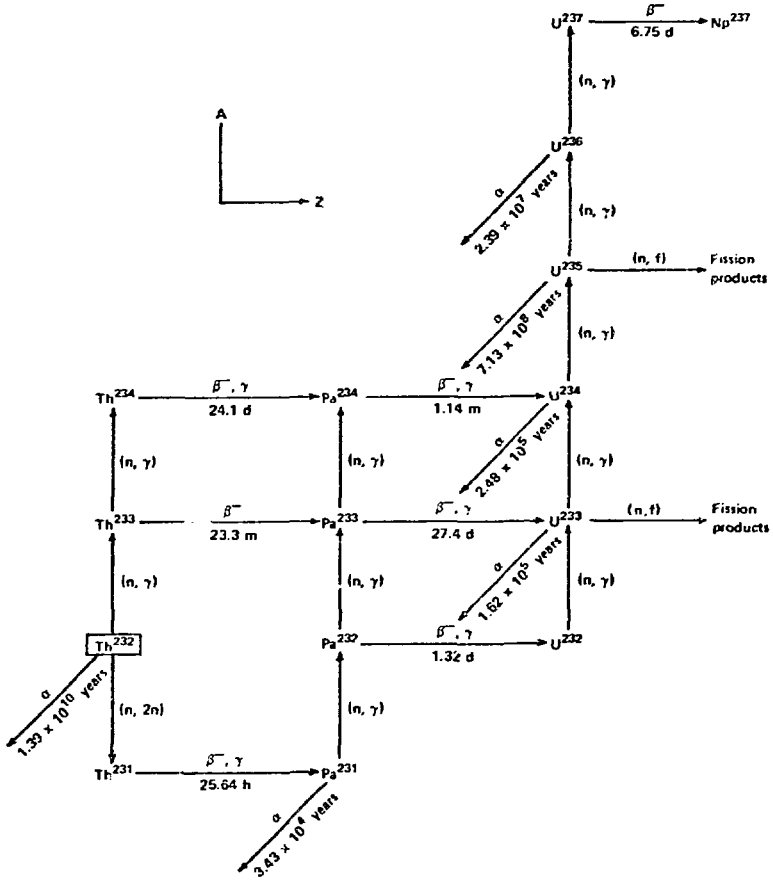


Fig. 1. Nuclide chains from thorium irradiation.

The ^{230}Th content of natural thorium varies between ∿5 and 100 ppm, depending on fuel source,[5] hence the ^{232}U content of the irradiated fuel will vary. The ^{232}U is an alpha emitter with a half-life of 72 yrs, and as such, poses no severe problems. However, one daughter in the decay chain, ^{208}Tl, emits a 2.6-MeV gamma ray, and for this reason all fuel manipulations of reprocessed ^{233}U produced in power reactors, including analytical chemistry, must be performed in shielded caves. The high radiation levels also adversely affect the performance of NDA instruments.

Another feature of the thorium fuel cycle that has serious safeguards implications is the ^{233}Pa intermediate (see Fig. 1). In conventional Purex (plutonium and uranium recovery by extraction) reprocessing an appropriate cooling time of at least 150 days between reactor discharge and reprocessing is required to permit decay of a large fraction of fission products. This is necessary to minimize problems in reprocessing associated with solvent heating and reagent degradation. For reprocessing of thorium fuels this cooling period must be observed not only for reprocessing but also for nuclear safeguards considerations. This safeguards need arises from the ^{233}Pa precursor of ^{233}U. Because almost 1 kg of 27-d ^{233}Pa is present per metric tonne of fuel discharged,[6] a cooling period of ~180 days is required to reduce the protactinium content to <10 g. For shorter cooling periods the unrecovered protactinium would decay to ^{233}U, which could subsequently be reprocessed. In a second recovery campaign this second batch of reprocessed ^{233}U would be essentially free of ^{232}U contamination, and hence of natural spiking from the ^{232}U daughters.

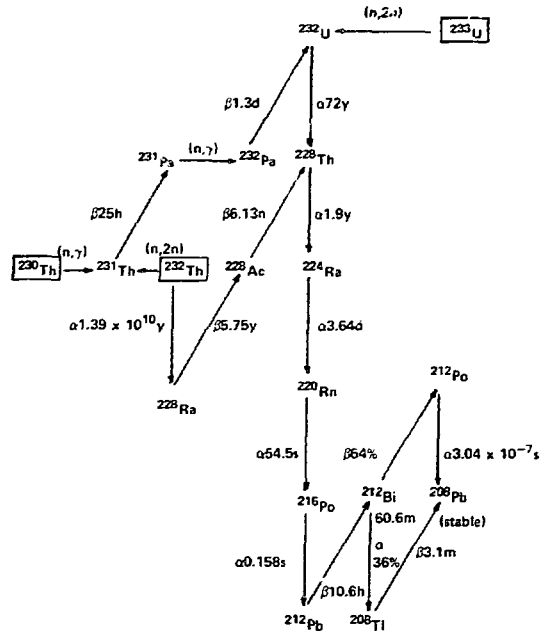


Fig. 2. Production and decay chain for ^{232}U.

In the Thorex (thorium and uranium recovery by extraction) or acid-Thorex processes protactinium is removed with the bulk of the fission products in the first extraction column. Flow sheets have been described for the recovery of ^{233}U or protactinium from the high-acid wastes. After a suitable aging time to permit decay of ^{233}Pa to ^{233}U, the uranium can be recovered by an

additional solvent extraction cycle. Protactinium can be recovered, without aging, by carbinol extraction[7] or by coprecipitation with sodium chromate[8] or manganese dioxide.[9] Protactinium also has been separated from short-cooled, irradiated thorium by adsorption on unfired Vycor glass.[10,11]

An important consideration in nuclear fuel use is the number of neutrons produced per neutron absorbed in the fissile isotopes (η). To achieve criticality in an ideal reactor (no neutron leakage or parasitic absorption) at least one neutron must be produced for each neutron absorbed ($\eta = 1$). If an ideal reactor is to breed fuel then at least two neutrons must be produced per absorption ($\eta = 2$): one to initiate the next fission and the balance to be absorbed in a fertile isotope to produce a fissile atom. A value of η between one and two indicates that the reactor converts some fertile material to fissile material but the reactor is a net user of fissile material. In practice ideal reactors cannot be built because of leakage, parasitic reactions, etc., and for sustained breeding η must be significantly >2. The value for η is a function of the energy of the neutron absorbed by the fissile isotope and is shown for ^{233}U, ^{235}U, and ^{239}Pu in Fig. 3.[12]

All three fissile isotopes have a sufficiently high η to breed at fast-neutron energies; however, only ^{233}U will breed with both thermal and epithermal neutrons. This has led to the development of the light-water breeder concept.[12] Even non-breeding ^{233}U-fueled thermal reactors have a higher conversion ratio than ^{235}U- or plutonium-fueled reactors, and this has given impetus to developing other thorium thermal reactor concepts such as the HTGR.

A. Thorium-Based Reactor Concepts

Some of the thorium-based reactor concepts will be discussed briefly to compare features that may be important in the development of safeguards systems for the accountability of strategic nuclear materials in fuel reprocessing.

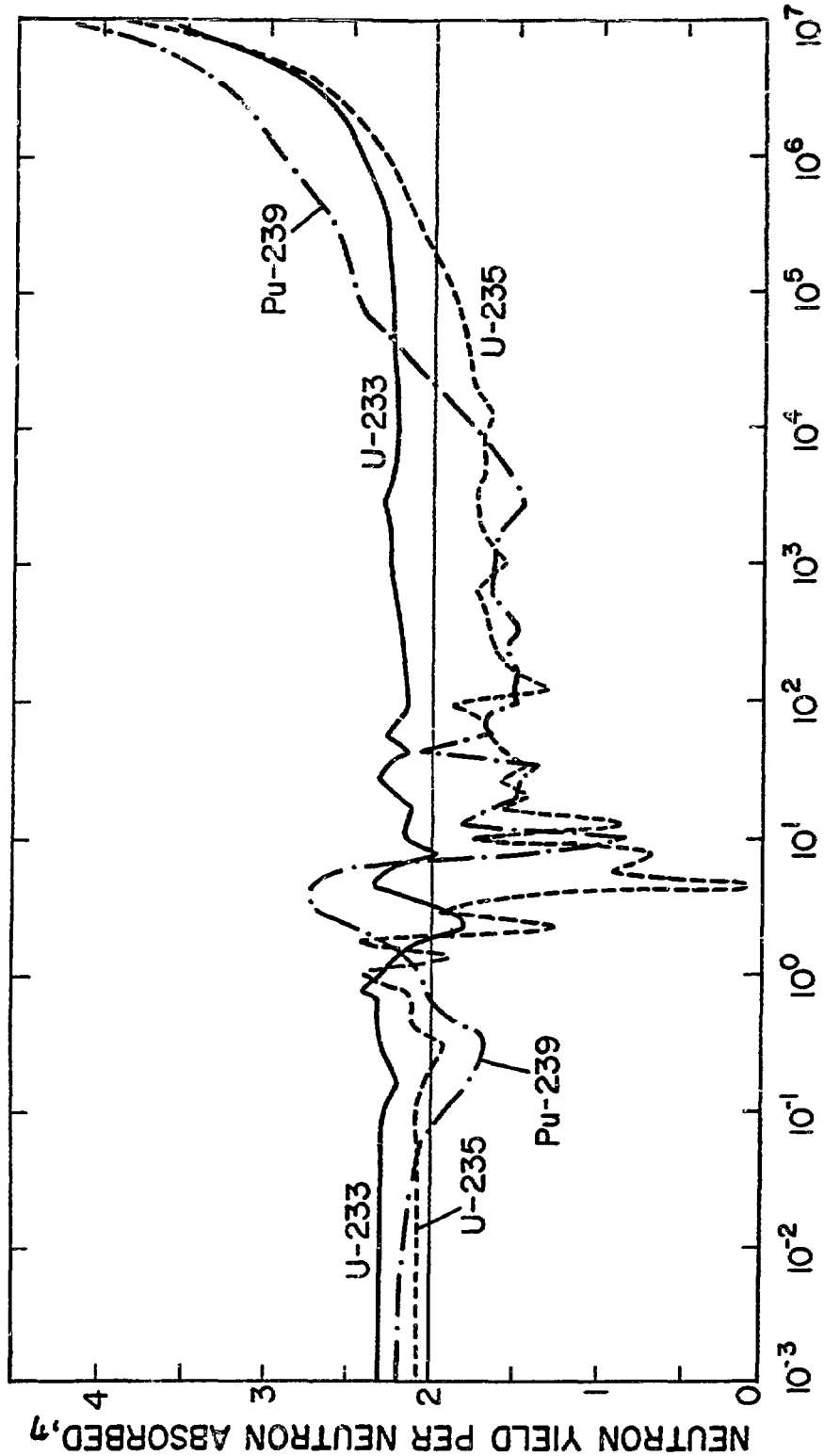


Fig. 3. Neutron yield per neutron absorbed, η, versus energy of neutron absorbed.

1. Light-Water Reactor. Conventional LWR fuel rods consist of $^{238}UO_2$ approximately 3% enriched in ^{235}U. In second-generation reactors some of the ^{235}U may be replaced by reprocessed plutonium.

The thorium LWR fuel cycle is initiated by replacing some of the ^{238}U with thorium to breed ^{233}U (Refs. 1 and 2). The amount of thorium that can be added is dictated by the nonproliferation requirement to maintain the ^{235}U enrichment below 20%. For first-generation reactors the fissile fuel consists of ^{235}U, with both ^{238}U and thorium as fertile material. Thus, plutonium as well as ^{233}U is formed, the plutonium content of the discharged fuel being 20-35% of the amount formed in conventional LWRs.

Second-generation reactors can be fueled with recovered ^{235}U and ^{233}U mixed with thorium, or plutonium mixed with thorium. Compositions for first-generation (fresh) and second-generation (recycle) fuels for the reference reactor are summarized in Table I.[13]

TABLE I

APPROXIMATE COMPOSITION OF REFERENCE THORIUM-BASED LWR FUELS

Isotope	Composition, %		
	Fresh	U Recycle	Pu Recycle
^{232}Th	77.87	74.57	95.09
^{232}U	---	0.0045	---
^{233}U	---	1.39	---
^{234}U	---	0.10	---
^{235}U	4.38	2.61	---
^{236}U	---	0.66	---
^{238}U	17.75	20.67	---
Pu (all isotopes)	---	---	4.91

Reprocessed uranium must be re-enriched prior to recycle. For the reference fuel cycle it is assumed that re-enrichment will be done by blending with highly enriched (50-93%) ^{235}U to decrease uranium feed and separative work requirements.[13] Because both highly enriched uranium and plutonium are used in thorium fuel-element fabrication, a basic assumption in preliminary design of the reference LWR fuel cycle is that the reprocessing, conversion, and fuel fabrication plants will be co-located in a secure area.

The reference thorium-based LWR fuel cycle has assumed co-mixing of fertile and fissile materials in the fuel and hence coprocessing of ^{233}U and ^{235}U in a single stream. One consequence of this mode of operation is the buildup of ^{236}U in the fuel by neutron absorption in ^{235}U. The ^{236}U is a parasitic absorber, resulting in eventual poisoning of the fuel. An alternative fuel concept is the seed-blanket, where the fissile ^{235}U and fertile thorium are placed in separate fuel rods in the reactor. The fuel rods are physically sorted prior to reprocessing. The fissile rods are chopped, dissolved in HNO_3, and uranium and plutonium are recovered by a Purex process. The fertile rods are chopped, dissolved in HNO_3 containing a low concentration of HF, and uranium and thorium are recovered using a Thorex process. Thus, ^{233}U and ^{235}U are maintained separately and the ^{235}U can be discarded when ^{236}U buildup becomes excessively high, possibly after two or three irradiation cycles.

One of the major difficulties in reprocessing thorium-based fuels compared to uranium-based fuels results from the relative insolubility of ThO_2. Magnesium oxide may be added to the fuel during fuel fabrication to facilitate ThO_2 dissolution.

The fuel cladding may be either stainless steel or Zircaloy. The latter provides some advantages in neutron efficiency and will be used in the reference design. This will produce some problems in fuel dissolution because the Zircaloy will dissolve in the HNO_3-HF mixture required to dissolve ThO_2, and the dissolved zirconium will complex the fluoride, rendering it ineffective in aiding ThO_2 dissolution. The dissolved

zirconium will also compete with the fission products in the first extraction cycle, reducing the decontamination efficiency and increasing the waste volumes.

2. Light-Water Breeder Reactor. The LWBR is a thermal breeder, similar in some respects to the LWR, but with a reactor core designed to optimize the neutron yield per fission, η, and to minimize neutron loss so that breeding can occur. Thus, the reactor becomes a net producer of fuel. The concept was developed by Westinghouse and a test core is being irradiated in the Shippingport reactor.[12]

Three initial loadings or prebreeder core concepts have been proposed. (Ref. 12, p. IX.G.1-4). The primary prebreeder concept uses low-enriched (10-15%) ^{235}U in thorium to provide an overall fissile concentration of 3-4%. The second concept uses a mixture of low-enriched uranium and plutonium to provide the required fissile content. The third concept uses high-enriched (90%) ^{235}U with ZrO_2 and a fissile concentration relative to thorium of 3-4%.

The breeder fuel assembly contains enriched (75-80%) ^{233}U in thorium in seed and blanket rods, with ThO_2 axial and radial reflectors. (Ref. 12, p. IX. G. 1-6). Fuel cladding for both prebreeder and breeder fuel elements is projected to be Zircaloy.

A significant difference between fast- and thermal-breeder fuels results from the lower penetration of neutrons into the fuel element in the thermal breeders. Thus, for the latter a significantly larger fraction of both fission and breeding occurs in the outer portions of the fuel rod, and the potential for cladding interactions with the bred uranium is greater. This may affect measurements of residual fissile material in leached hulls. Reprocessing of LWBR fuels would be similar to LWR fuels.

3. Fast-Breeder Reactor. As with the uranium-plutonium fuel cycle, fast breeders can be designed around the uranium-thorium cycle, and a concept based on a mixed uranium-thorium-plutonium-oxide fuel has been described.[14] Fast-breeder fuels consisting of mixed oxides and metal alloys have been studied.[15]

Cladding for FBR fuels could be stainless steel or Zircaloy. Reprocessing FBR oxide fuels would be similar to LWR fuels, but probably with reduced throughputs if higher burnups are used. Metal fuels may require modification in dissolution procedures.

4. High-Temperature Gas-Cooled Reactor. The HTGR[16] has been under development both in the United States and abroad since the 1950's. Its attractiveness lies in lower fuel costs, partly due to the elimination of cladding, and a higher conversion ratio than in LWRs. Both fissile and fertile fuels are present as small carbon-coated particles (microspheres or beads) distributed throughout a graphite fuel matrix.

The initial loading of the reactor core uses ^{235}U as the fissile material, with an enrichment of up to 93% (referred to as 1M fuel). In addition to the 93% enrichment (high enriched), enrichments of 20-30% (medium enriched) and 10% (low enriched) are being considered. The Th/U ratio is nominally between 5 and 10, depending on reactor design. The US HTGR reactors such as Fort St. Vrain are designed for 90% burnup of the ^{235}U in the initial high-enriched loading. During this time (~6 yrs) 70 atoms of the ^{232}Th have been converted to ^{233}U per 100 atoms of ^{235}U fissioned, and approximately half of this ^{233}U has undergone fission.

The fuel from the initial loading still contains significant amounts of ^{235}U when the fuel is discharged, and recovery of the ^{235}U value is desirable. However, during burnup significant amounts of ^{236}U, a neutron poison, are produced. Hence, it is planned that this uranium will be reprocessed only once (referred to as 25R fuel); the second discharge will be discarded without reprocessing (referred to as 25RW or 25RS fuel), which, because of its ^{236}U content, has a marginal fuel value. Some plutonium also is produced in the initial fissile loading from neutron absorption by ^{238}U as well as successive capture in ^{236}U, with the Pu/U ratio ~0.005 to 0.01. The plutonium produced can be coprocessed with the recovered uranium and used to

increase fissile content of 25R fuel, or it can be cycled to high-level liquid waste with the fission products.

A third type of fissile fuel consists of the recovered ^{233}U from fertile fuel and is referred to as 23R fuel. It is anticipated that approximately one-half of subsequent loadings of the reactor will be with 23R fuel.

The fissile fuel particles consist of a UC_2 (or UO_2) core surrounded by a buffer and a three-layered coating. The buffer layer is porous graphite to absorb fission-product gases, the inner layer is dense pyrolytic graphite, the intermediate layer is SiC, and the outer layer consists of dense pyrolytic graphite. The SiC serves two purposes: it helps to retain fission products within the kernel, and it aids in subsequent separation of fissile and fertile particles during reprocessing. This triple layering is referred to as Triso coating.

A German pebble-bed HTGR uses graphite spheres ~6 cm in diameter for fuel. The reactor is designed for continuous refueling, and can be operated on low-enriched ^{235}U or uranium-thorium fuels.[17] Each fuel ball contains ~1 g of ^{235}U (or ^{233}U) and 5 g of thorium, either as the oxides or carbides.[18] The fuel matrix compositions and fabrication techniques are similar to those used in conventional HTGRs.

5. Heavy-Water Reactor. The primary development of the HWR has taken place in Canada, and has been commercialized worldwide with the CANDU reactor. The fuel consists of UO_2, and generally is considered a "throwaway" fuel cycle, i.e., no attempt is made to recover the converted plutonium. Studies are being performed to substitute ThO_2 containing enriched ^{235}U as fuel for the CANDU.[19] Reprocessing of the fuel will be required to recover the ^{233}U.

B. Reprocessing

The reprocessing[16] of uranium-thorium fuels differs significantly from reprocessing in the uranium-plutonium cycle. Two types of headend will be required: a chop-leach process for oxide

fuels such as in the reference LWR or LWBR, and a burn-crush process for HTGR-type graphite fuels. The oxide can be dissolved in HNO_3 if only uranium and plutonium are present, but addition of a small amount of HF in the HNO_3 is required if thorium is present. Magnesium oxide is added to ThO_2 fuels in the reference process to further facilitate dissolution.[2]

Solvent extraction for first-generation fissile fuel is performed using a conventional Purex scheme. The thorium-based fertile fuels require a Thorex extraction process. Second-generation fuels can be reprocessed in a modified Thorex process with separate product streams for thorium, uranium, and plutonium.

1. Headend. The chop-leach process has been developed and tested extensively for conventional LWR fuels.[20] Approximately 1 metric ton (MT) of oxide fuel is chopped into pieces 2.5-13 cm (1-5 in.) in length, producing ~290-390 kg of Zircaloy and/or stainless-steel hulls. It is anticipated that crimping of fuel rods during chopping will be minimal due to irradiation embrittlement of fuel-rod cladding. Some fines will be produced during chopping, consisting primarily of Zircaloy and metallic noble-metal fission-product ingots that may contain alloyed uranium and plutonium.[21]

For the graphite-based fuels the spent fuel elements, which consist of graphite containing a mixture of fertile and fissile beads, are crushed to pieces that can be handled in a fluidized-bed burner. The graphite/thorium ratio is >200, and burning is the only practical means for removing the large amounts of carbon. Burning is performed in a fluidized bed at ~825°C removing the unprotected carbon particle coatings as well as the graphite fuel matrix. An alternative concept calls for whole-block burning of fuel elements without crushing. In either case, burn rate must be controlled to prevent thermal cracking of the SiC coating on fissile beads, which would result in crossover of ^{233}U and ^{235}U.[16]

After the carbon has been removed, the fissile and fertile particles are separated by pneumatic classification. The

uncoated fertile ThO_2 particles have a density of 10, whereas the SiC-coated UC_2 particles have a density of 3. Using a differential density method, separation is achieved with a crossover of <1% of fertile and <5% of fissile particles.

In an alternative separations scheme, the uncoated fertile particles are dissolved directly after burning. The SiC-coated fissile particles are then crushed and the UC_2 cores are dissolved separately for reprocessing.

2. Dissolution. For first-generation uranium-based fuels the chopped fuel segments fall into a dissolver containing hot 3 M to 8 M HNO_3 (and gadolinium nitrate for criticality control), which dissolves the solid UO_2-PuO_2-fission product matrix.

Chopped thorium-based fuel will be dissolved in ~12 M HNO_3-0.05 M HF.[1] Some Zircaloy cladding also will dissolve, complexing the fluoride and retarding the dissolution rate. Addition of MgO to the ThO_2 fuel during fabrication is being considered for the reference process to facilitate dissolution.

For graphite-based fuels the oxide produced from the burner is dissolved in a solvent 11-13 M in HNO_3, ~0.05 M in HF, and ~0.1 M in $Al(NO_3)_3$ (Thorex solution). The solution is centrifuged to remove solids, which presumably consist primarily of metallic fission product ingots and any intact triso-coated fissile particles. The metallic ingots could contain some ^{233}U.

3. Solvent Extraction. A modified Thorex process having separate product streams for thorium, uranium, and plutonium is proposed for the reference facility. The process is described in more detail in Chap. III.

4. Wastes. Solid, liquid, and gaseous wastes are generated from reprocessing oxide or graphite-based fuels. Gaseous wastes do not present safeguards problems and are not considered.

a. Solid Wastes. The primary solid wastes from reprocessing LWR-type oxide fuels are the hulls and miscellaneous

packaged process wastes. The high-level waste hulls are monitored for fissile content using either gamma-ray or neutron-interrogation techniques.

Solid wastes from reprocessing HTGR-type graphite fuels consist of fines collected on filters during crushing, SiC hulls, and spent ^{235}U fuel elements. The fines on HEPA filters may contain ∿0.1% of the actinides in the fuels (Ref. 22, p. 15). However, another study showed that as much as 1% of the original uranium was found on the filters, and leaching with HNO_3 removed less than 50% of the uranium (Ref. 5, pp. 64-66).

The centrifuge sludge containing the SiC hulls from fissile fuel particles and metallic ingots of noble-metal fission products, are expected to contain <10% of the fission products and <0.1% of the uranium (Ref. 22, pp. 16; Ref. 24). However, a recent study showed that as much as 0.6% of the uranium may remain undissolved with the centrifuge solids.[23] If this is the case, an accountability measurement must be made, or an additional reprocessing step must be added to recover the uranium. In any event, additional work is required to characterize the form of the uranium in the insoluble material.

The 25RW fuel will contain ∿4% of the uranium as ^{235}U; however, the high ^{236}U content (∿70%) renders it unusable for further recycle. The beads can be stored as solids in high-level wastes or stored as vitrified-matrix solid high-level wastes. In either case, accountability measurements are required. Approximately 64% by weight of the nuclides present are actinides, and ∿10% of the actinides are plutonium.

b. Liquid Wastes. Liquid wastes from both LWR or HTGR reprocessing plants are expected to be similar and are classified as low, intermediate, and high level. Low-level liquid wastes (LLLW) are concentrated, then batch-transferred to high-level wastes after measurement of SNM content. Intermediate-level liquid wastes (ILLW) originate from the solvent and acid-purification systems. These are measured for SNM content, then stored in the ILLW storage tank. High-level liquid wastes (HLLW) are

generated from LLLW concentrate, fission product partitioning, and centrifuge sludge and can contain appreciable quantities of solids. These are stored in HLLW storage tanks after measurement of SNM.

III. THE REFERENCE PROCESS

The reference process used for this study combines the headend and plutonium purification system from an LWR Purex fuel reprocessing plant with an HTGR Thorex solvent extraction system. The preliminary conceptual process produces separate streams of thorium, uranium, and plutonium as nitrate solutions. The basic unit processes of the thorium fuel reprocessing flowsheets are presented in Fig. 4. Technology for the fission product decontamination and uranium partitioning, plutonium-thorium partitioning, and uranium purification are derived from a conceptual design developed by General Atomic.[25] The remaining unit processes are based on Allied General Nuclear Services technology for the Barnwell Nuclear Fuels Plant.[20]

A. Design Capacity

The reference plant is designed to receive and process irradiated uranium-thorium-oxide fuels. The plant is sized to process 5 metric tonnes of heavy metal per day (MTHM/day) or 1500/MTHM/yr of fuel with an average burnup of 33 000 MWd/MTHM. The fuel is assumed to be Zircaloy or stainless steel clad having a configuration similar to that of a typical LWR fuel bundle. Composition of typical as-received fuel is given in Table II.

B. Headend

1. Fuel Receiving and Storage Disassembly. A process flow diagram for the fuel receiving, storage, and disassembly operation is presented in Fig. 5. The spent-fuel assemblies arrive in shielded casks via rail or truck. These massive casks, which may

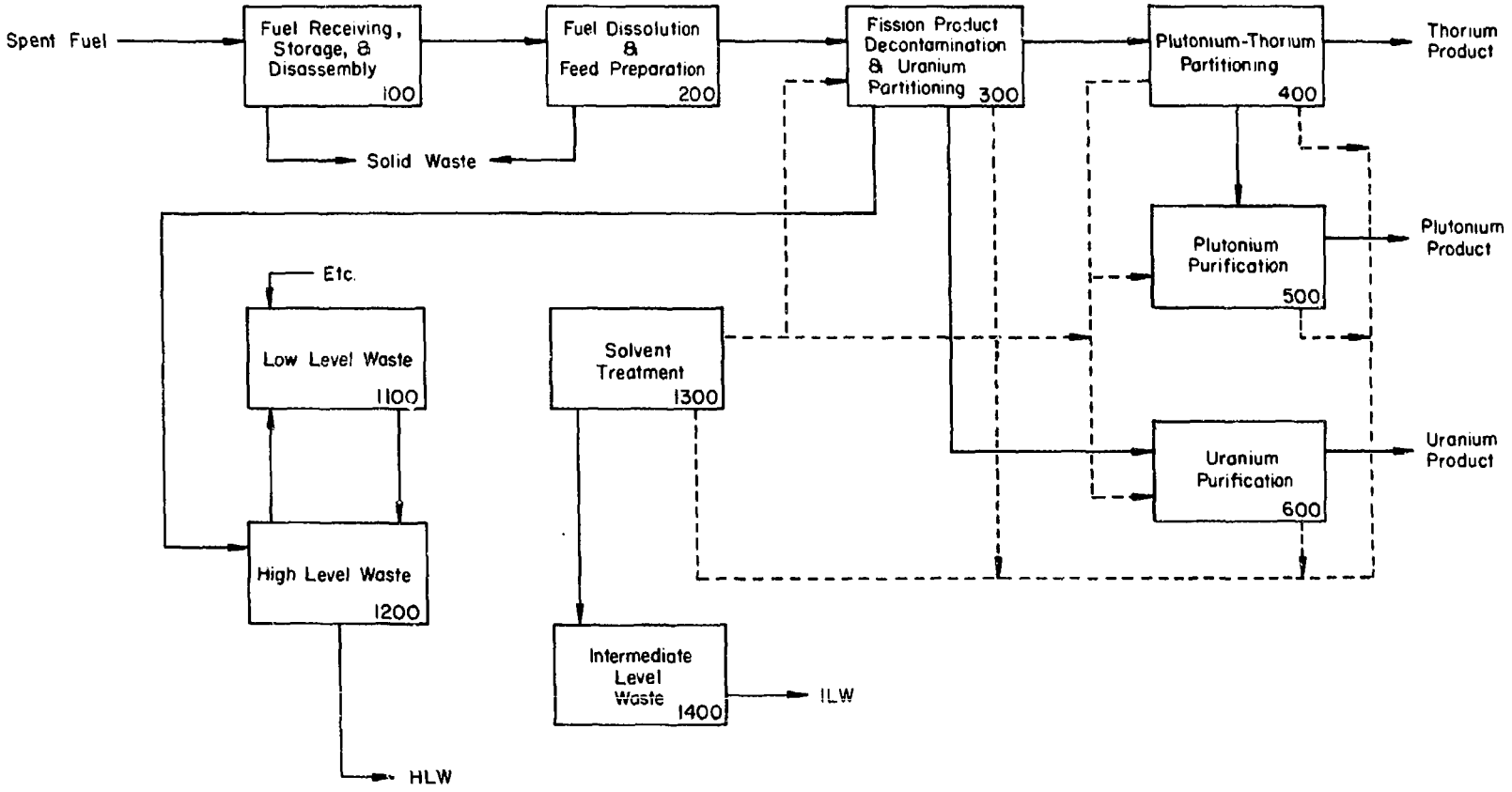
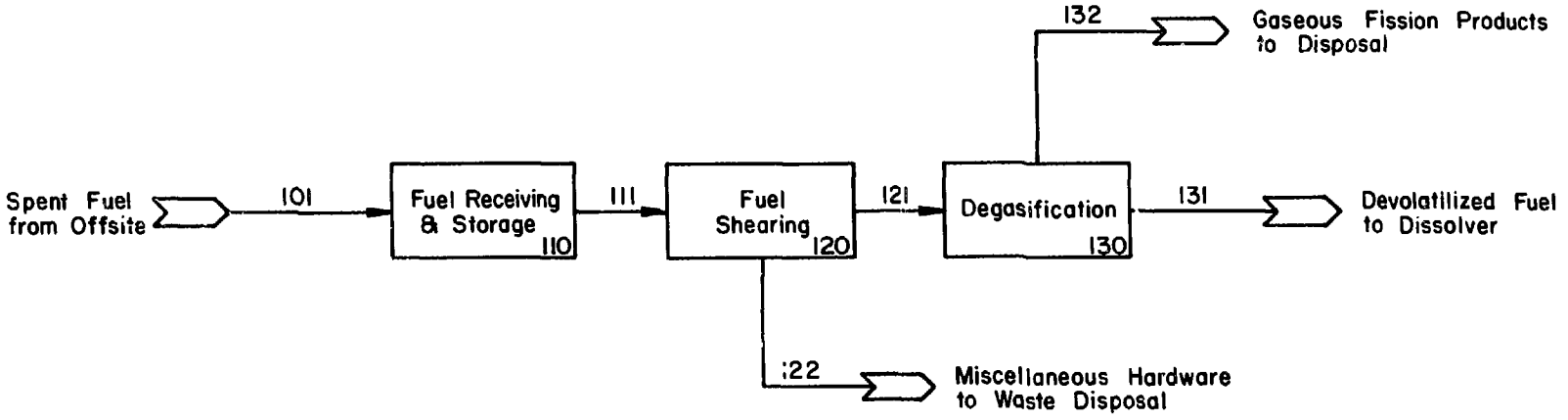


Fig. 4. Flow schematic: thorium fuels reprocessing.



Stream number	101	111	121	122	131	132
Stream name	Spent Fuel from Reactor	Fuel Bundles	Sheared Fuel	Misc. Hardware	Dissolver Feed	Volatile Fission Prods.
Kilograms/h						
Kilograms/batch	45,500	455			1,460	
Thorium, kg		230			730	
Uranium, kg		85			265	
Plutonium, kg		1			4	
Fission Prods.,kg		10			30	
Hulls, kg		90			290	
Misc. Hrdwre,kg		11				

Fig. 5. Process flow diagram: fuel receiving, storage, and disassembly.

TABLE II

FUEL COMPOSITION IRRADIATED URANIUM-THORIUM FUEL
(33 000 MWd/MTHM)

Component	kg/MTHM[13,26]	
Thorium	789	
Uranium		207
U - 232	0.03	
U - 233	11.7	
U - 234	.8	
U - 235	15.9	
U - 236	5.2	
U - 238	173.5	
Plutonium		4.0
Pu - 238	0.13	
Pu - 239	2.42	
Pu - 240	0.67	
Pu - 241	0.59	
Pu - 242	0.17	

weigh up to 100 tons, provide radiation shielding to prevent excessive exposure to operations personnel, prevent release of hazardous materials should an accident occur during transit, and provide a heat sink and thermal dissipation for the heat generated by the spent fuel. The massive casks and the specialized equipment necessary for transport and handling also provide pnysical security for their contents.

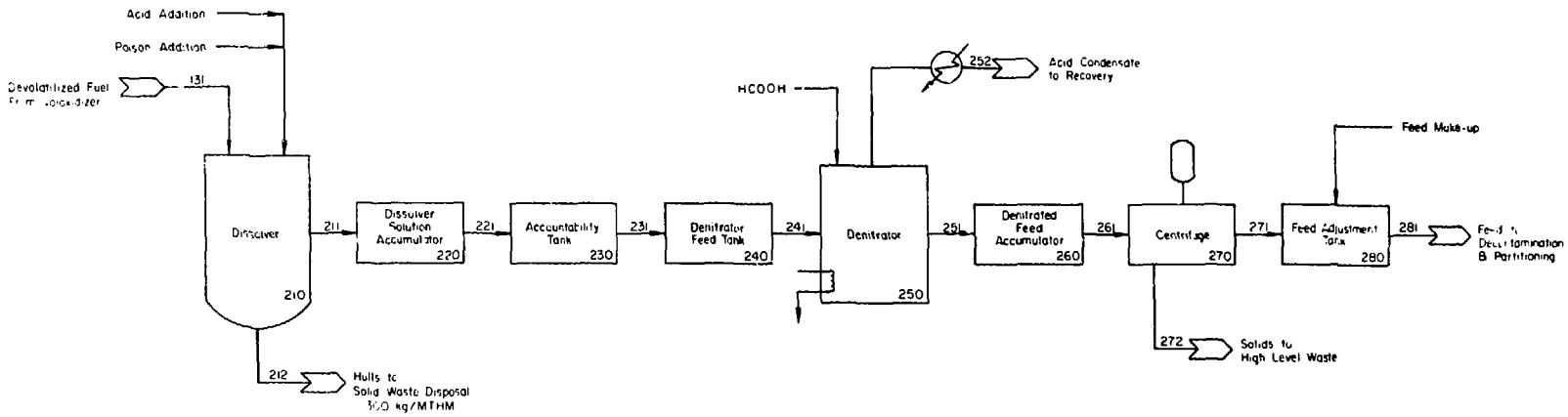
Upon receipt at the facility, the cask and vehicle are monitored for external contamination and washed to remove surface dirt. The cask is removed from the vehicle to a test and decontamination pit to check the condition of the fuel and cask coolant. A cask cool-down system is used to reduce cask and fuel temperatures to below boiling. The cask is moved to the cask-unloading pool and is lowered to the bottom of the pool where the cask is opened and the fuel is removed. The fuel is transferred to the fuel-storage pool and is stored until ready for reprocessing. The fuel assembly remains in the storage pool as required for decay and cooling prior to reprocessing.

When ready for processing, the fuel assemblies are remotely transferred from the storage pool to a mechanical shear where they are chopped into small segments. The chopped elements are then heated in a moist oxygen atmosphere to remove tritium and other volatile fission products (Voloxidation).

2. Fuel Dissolution and Feed Preparation. Figure 6 presents a flow diagram for fuel dissolution and feed preparation. Chopped fuel segments from the voloxidation system are charged to a dissolver containing hot, concentrated HNO_3. Fluoride may be added to the dissolver solution to aid in dissolution. The dissolver solution is transferred to an accountability tank for sampling and inventory control. The dissolver liquor is prepared from fresh HNO_3 makeup, which contains recycled dissolver solution and hull-rinse liquor.

The solid hulls, consisting primarily of stainless steel or Zircaloy fuel-element hardware and tubing remnants, are transferred to solid-waste disposal. The cladding hulls are rinsed, monitored for fissile material, packaged, and transferred to the solid-waste storage. These hulls may contain up to 0.1% of the total incoming thorium, uranium, and plutonium.

Gases generated during dissolution are directed to the off-gas treatment system, which removes particulates, radioiodine, and nitrogen oxides.



Stream number	131	211	221	231	241	251	252	261	271	272	281
Service	Fuel from Voloxidizer	Dissolver Solution	Dissolver Solution	Dissolver Solution	Denitrator Feed	Denitrated Solution	Acid Condensate	Denitrated Solution	Clarified Solution	Centrifuge Solids	HAF
Kilograms/h											
Kilograms/batch	1,460										
Liters/h					1,500	760		760	760		760
Liters/batch		7,165	7,165	7,165							
Thorium, g/L		102			102	200					200
Uranium, g/L		37			37	73					73
Plutonium, g/L		0.5			0.5	1.0					1.0
Fission Prods., g/L		1.5			1.5	3					3
HNO_3, M		12.0			<1.0		10.0				1.0

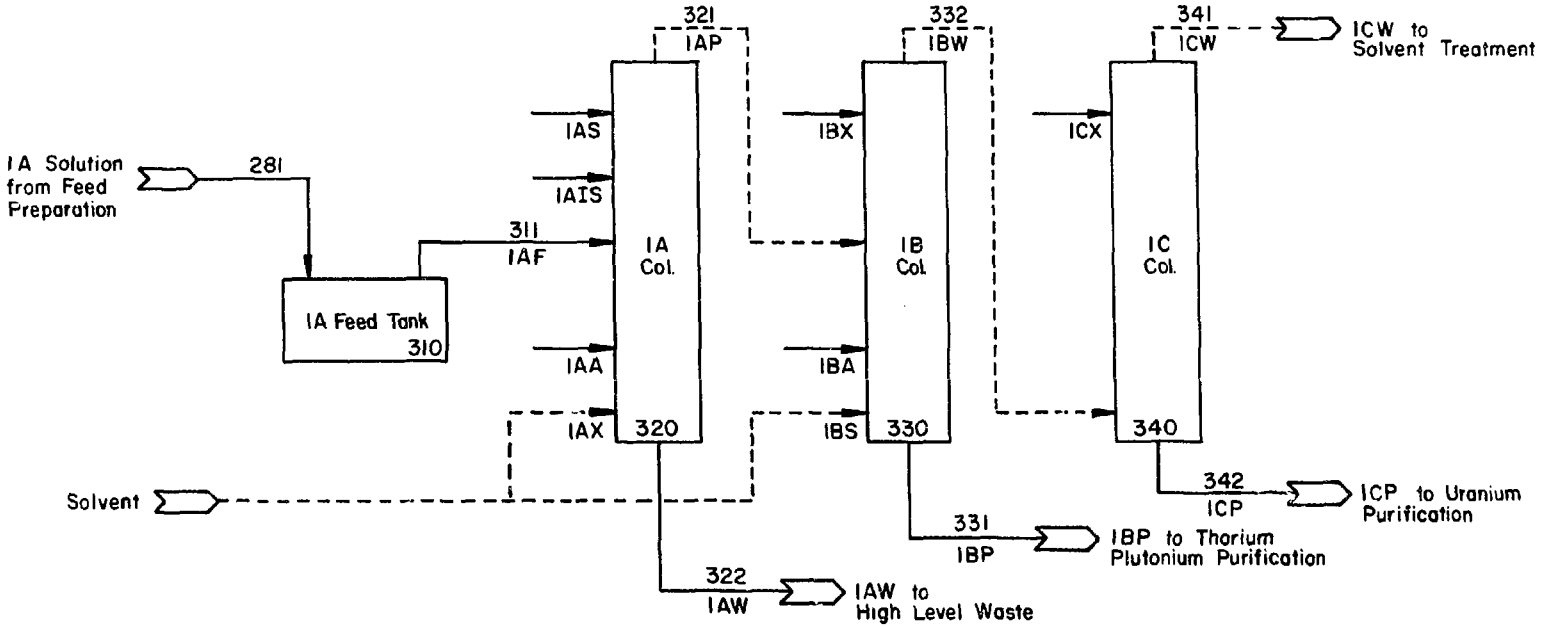
Fig. 6. Process flow diagram: fuel dissolution and feed preparation.

After accountability measurements, the highly acidic dissolver solution is transferred to a continuous denitrator, where the acid concentration is reduced to less than 1.0 M by boiling in the presence of formic acid. The low-acid denitrator product is cooled, centrifuged to remove solids, and adjusted to approximately 0.9 M Th and 0.5 to 1.0 M H^+ for use as feed to the subsequent solvent-extraction systems.

C. Solvent Extraction

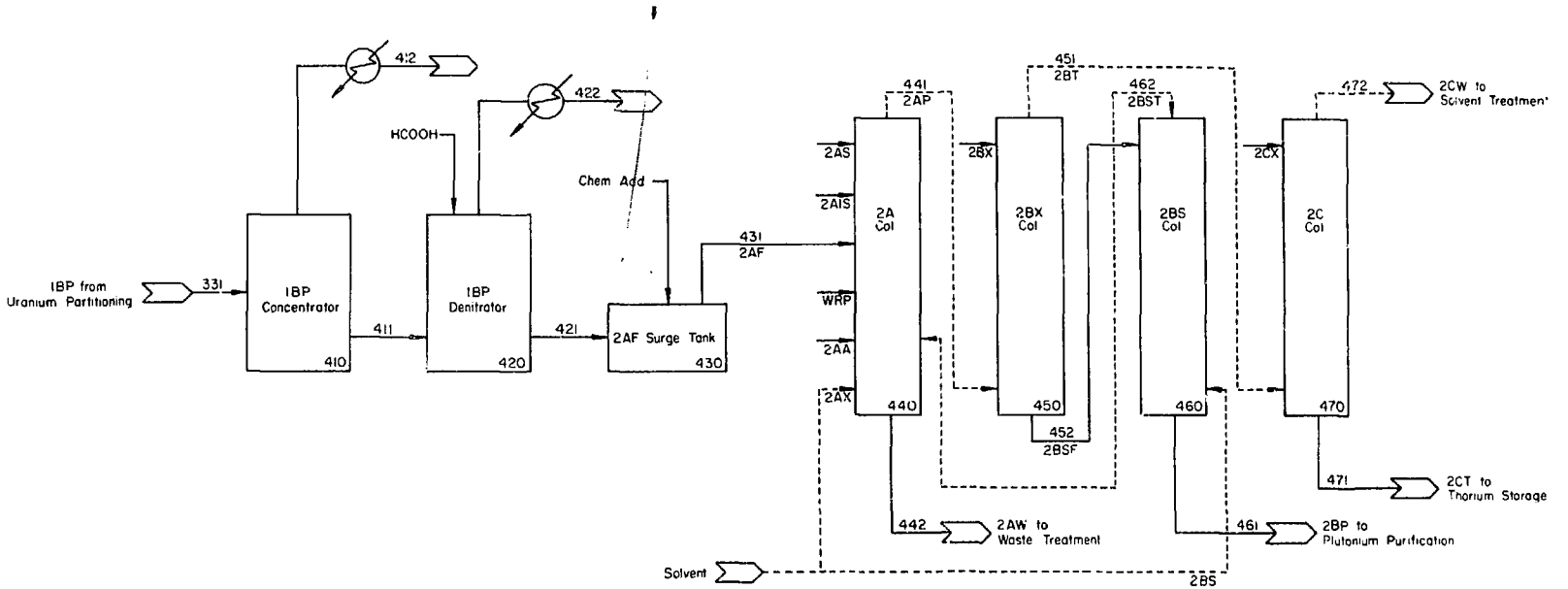
1. Fission-Product Decontamination and Uranium Partitioning. Figure 7 presents a flow diagram for fission-product decontamination and uranium partitioning. The 1AF acid feed solution is contacted with an organic extractant consisting of 30% TBP in normal paraffin-hydrocarbon diluent (dodecane). The TBP preferentially extracts the thorium, plutonium, and uranium, leaving about 99% of the fission products in the aqueous solution. The organic stream from the contactor passes through a pulsed extraction column, where 0.25 M aqueous HNO_3 solution strips thorium and plutonium from the organic solution. The remaining organic phase bearing the uranium flows to the 1C column where the uranium is stripped from the organic into the aqueous phase.

2. Plutonium-Thorium Partitioning. Figure 8 illustrates the plutonium-thorium partitioning system. The 1BP stream enters the 1BP concentrator, where the plutonium and thorium concentrations are increased by evaporation. The concentrated Pu/Th solution overflows the 1BP concentrator into a feed adjustment tank where the acidity is increased to about 2.0 M by acid addition. The 2AF then passes to the 2A column where the plutonium and thorium are extracted into organic solvent. The aqueous stream (2AW) exiting the 2A column contains a significant concentration of fission products and is routed to high-level waste processing. The organic stream, (2AP), which contains the extracted plutonium and thorium, overflows to the 2B column.



Stream number	281	311	321	322	331	332	341	342
Service	IAF	IAF	IAP	IAW	IBP	IBW	ICW	ICP
Kilograms/h								
Liters/h	760	760	5090	1550	3055	6005	6005	3015
Thorium, g/L	200		30	< 1	50			
Uranium, g/L	73		11	$< 10^{-2}$	Tr	9		18
Plutonium, g/L	1.0		0.1	$< 10^{-3}$	0.25			
Fission Prods., g/L	3		< 0.1	1.5				
HNO_3, M	1.0			2.0	0.25			0.10

Fig. 7. Process flow diagram: fission product decontamination and uranium partitioning.



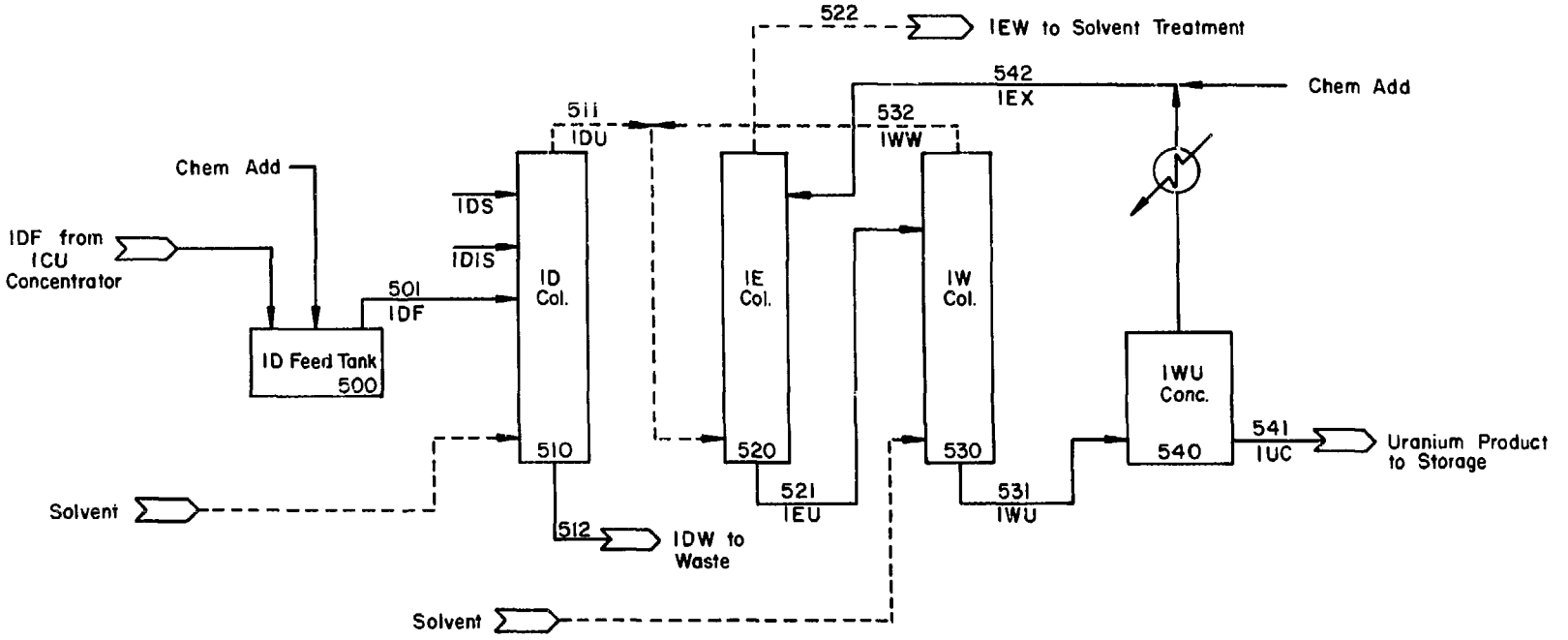
Stream number	331	411	412	421	422	431	441	442	451	452	461	462	471	472
Service	1BP	1BP	1BD	2AF	2AD	2AF	2AP	2AW	2BT	2BSF	2BP	2BST	2CT	2CW
Kilograms/h														
Kilograms/batch														
Liters/h	3055	1525	1530	1525	0	1525	4515	2195	5735		610		3220	5735
Liters/batch														
Thorium, g/L	50	100		100		100	35	$<10^{-1}$	25		<0.2		47	$<10^{-2}$
Uranium, g/L	Tr	Tr		Tr		Tr								
Plutonium, g/L	0.25	0.5		0.5		0.5	0.2	$<10^{-3}$	0.1		1.26			$<10^{-4}$
Fission Prods, g/L														
HNO_3, M	0.25	0.2				2.0		0.5			2.0		0.7	

Fig. 8. Process flow diagram: plutonium-thorium partitioning.

Trivalent plutonium is less soluble in the solvent than is thorium. This difference is exploited to achieve partitioning between the plutonium and thorium by control of HNO_3 concentration and relative flow rates of the various input streams and addition of a reductant. The plutonium is stripped from the 2AP by a stream (2BX) of 2 M HNO_3, 0.1 M $Fe(NO_3)_2$, and 0.2 M N_2H_4. The thorium-bearing organic phase (2BT) passes to the 2C column where the thorium is stripped into a 0.7 M HNO_3 stream (2CT). The 2CT stream, devoid of plutonium, is sent to thorium concentration and storage.

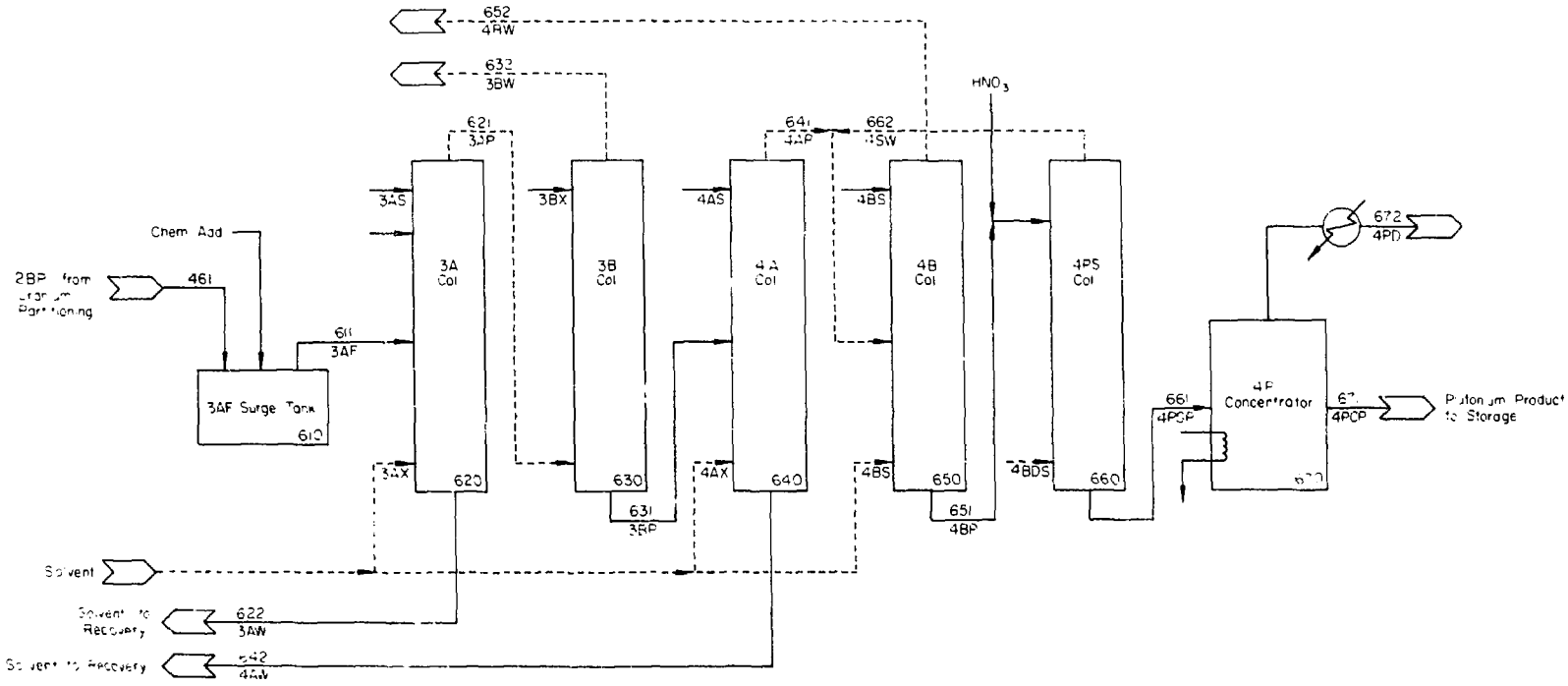
3. Uranium Purification. Final uranium purification is achieved in a third solvent extraction cycle illustrated in Fig. 9. Nitric acid is first added to the 1CU stream to provide the necessary salting strength. Uranium-bearing solutions are purified and concentrated by extraction into organic solvent in the 1D column, stripping into an aqueous phase in the 1E column, and finally washing to remove trace organics in the 1W column. After washing, the 1WU stream is concentrated to 2.0 M uranium and routed to storage.

4. Plutonium Purification. Plutonium is purified as shown in Fig. 10. Plutonium in the aqueous stream from the plutonium-thorium partitioning cycle is reoxidized to the extractable tetravalent state with nitrogen tetroxide and is preferentially extracted into the TBP-organic solution in the 3A column. The plutonium-bearing organic stream is scrubbed with HNO_3 to remove extracted ruthenium, zirconium, and niobium. The organic stream passes through a stripping column (3B) where further washing with dilute HNO_3 strips the plutonium back into the aqueous phase. The extraction-scrubbing sequence is repeated in another plutonium cycle (4A and 4B columns) for further decontamination from fission products. The plutonium-nitrate solution is washed with an organic diluent stream to remove traces of TBP and then is concentrated to 250 g/L. The plutonium-nitrate product solution is sampled and analyzed and then is stored in geometrically favorable tanks.



Stream number		501	511	512	521	522	531	532	541	542
Service	ICU	IDF	IDU	IDW	IEU	IEW	IWU	IWW	IUC	IEX
Kilograms/h										
Kilograms/batch										
Liters/h	1225	1225			1060	3730	1060			
Liters/batch										
Thorium, g/L	$<10^{-5}$	$<10^{-5}$								
Uranium, g/L	45	45					52		475	
Plutonium, g/L										
Fission Prods., g/L										
HNO_3, M		4.1					0.25			

Fig. 9. Process flow diagram: uranium purification.



Stream number	461	611	621	622	631	632	641	642	651	652	661	662	671	672
Service	2BP	3AF	3AP	3AW	3BP	3BW	4AP	4AW	4BP	4BW	4PSP	4SW	4PCP	4PD
Kilograms/h														
Kilograms/batch														
Liters/h	610	700	100	530	55	60	35	85		40	15	12	3.1	
Liters/batch														
Thorium, g/L	.02	.02	.05		.01	Tr	.02			.02				
Uranium, g/L														
Plutonium, g/L	1.26	1.1	8	Tr	1.4	Tr	2.2	0.1			5		250	
Fission Prods, g/L														
HNO_3, M	2.0	3.2		3.0	0.5			3.0		0.05	4		3.0	

Fig. 10. Process flow diagram: plutonium purification.

D. Waste Treatment

1. Liquid Wastes. Spent solvents from the solvent-extraction systems are washed with dilute acid to remove fission products and with sodium carbonate to remove degraded TBP and other organics. The radioactive aqueous-waste streams from the solvent-extraction cycles and aqueous wastes from solvent treatment are concentrated in the high-level or low-level waste concentrators. The acidic, high-level, concentrated bottoms are stored in cooled stainless steel waste tanks, and the overheads are fed to the low-activity waste concentrator. The overheads from the low-activity waste concentrators are fed to an absorption column to recover HNO_3 and these overheads (primarily water) are recycled as process water, or are sampled and released to the stack. The recovered acid is used in process steps where the residual radioactivity can be tolerated. The bottoms from the low-activity waste concentrator are fed to the high-activity waste concentrator.

Miscellaneous process waste streams containing salts and fission products are acidified, concentrated in a general-purpose concentrator, and stored as intermediate-level liquid waste. The condensed overheads from the general-purpose concentrator are vaporized to the stack.

Miscellaneous low-level liquid waste streams such as waste water from fuel storage, plant floor sumps, and cold chemicals are sent to a service concentrator where the water is evaporated and discharged to the stack. Miscellaneous waste streams containing salts and fission products (<1 Ci/L and no appreciable uranium or plutonium) are acidified, concentrated, and stored with the intermediate-level liquid waste.

2. Gaseous Wastes. Off-gases from the dissolver are scrubbed with circulating mercuric-nitrate nitric-acid solution to remove radioactive iodine, and then are treated in an absorber

to convert nitrogen oxides to nitric acid suitable for recycling. The dissolver off-gas and vessel off-gas streams are combined and passed through a second iodine scrubber containing mercuric nitrate, then through iodine adsorption beds and random holdup beds, and finally through high-efficiency filters before being released to the stack.

3. Solid Wastes. Waste solidification will be required in the future. Liquid wastes will be stored pending completion of a solid-waste conversion facility.

IV. THE SAFEGUARDS SYSTEM

The safeguards system must be incorporated into the plant during early design stages. The design should consider process and safeguards requirements for both systems operation and SNM measurements. Some of the safeguards features are considered in the following sections.

A. System Structure

The basic management, control, and coordination structure of safeguards systems for domestic nuclear fuel cycle facilities has been described in several earlier reports.[27-33] This report does not address directly the problems of international safeguards or interactions with the IAEA. However, it should be recognized that the safeguards system structure discussed here would form the backbone of an effective operator's safeguards system in either national or multinational fuel cycle facilities. Such a safeguards system would significantly ease the application of IAEA safeguards.

A comprehensive safeguards strategy includes three functions: (1) exclusion of all unauthorized persons from the facility, with further selective exclusion of others from sensitive areas within the plant; (2) control of all activities involving strategic nuclear materials (SNM) so that each such activity is

specifically authorized; and (3) confirmation that all materials are contained in their proper locations. The system for implementing that strategy must operate without unnecessary disruption of plant operations, compromise of safety requirements, or infringements on employee working conditions.

The following describes a system structure for accomplishing these goals. More detail can be found in Ref. 34 as well as in earlier reports.[27-33]

The general block diagram of the facility and the safeguards system is shown in Fig. 11, with those functions directly related to the process enclosed in heavily outlined boxes. The process-control function is distributed along the process and item-operations lines in the form of local controllers, one for each portion of the process. The actions of the process controllers are supervised by the process-control coordination unit (PCCU). This hierarchical control is usually implemented through setpoint commands in which the operating point of each portion of the process is specified by the PCCU on the basis of operational authorizations, process-operation considerations, and safety. Many portions of the process may be self-regulating, requiring only that they be monitored for limit conditions.

The PCCU is also responsible for implementing safeguards-related recommendations that affect process operations. This implementation is necessary to ensure effective compliance from both the safeguards and process-control viewpoints. The materials measurement and accounting system (MMAS) and the PCCU also exchange process-related information to improve process operation and safeguards effectiveness.

The safeguards coordination unit (SCU), described in more detail in Refs. 30 and 31, supervises SNM safeguarding in the facility. As the focal point for safeguards decisions, this unit interacts with management and process-control coordination to ensure effective safeguards. Safeguards coordination must be as simple and reliable as possible, and its decision-making function

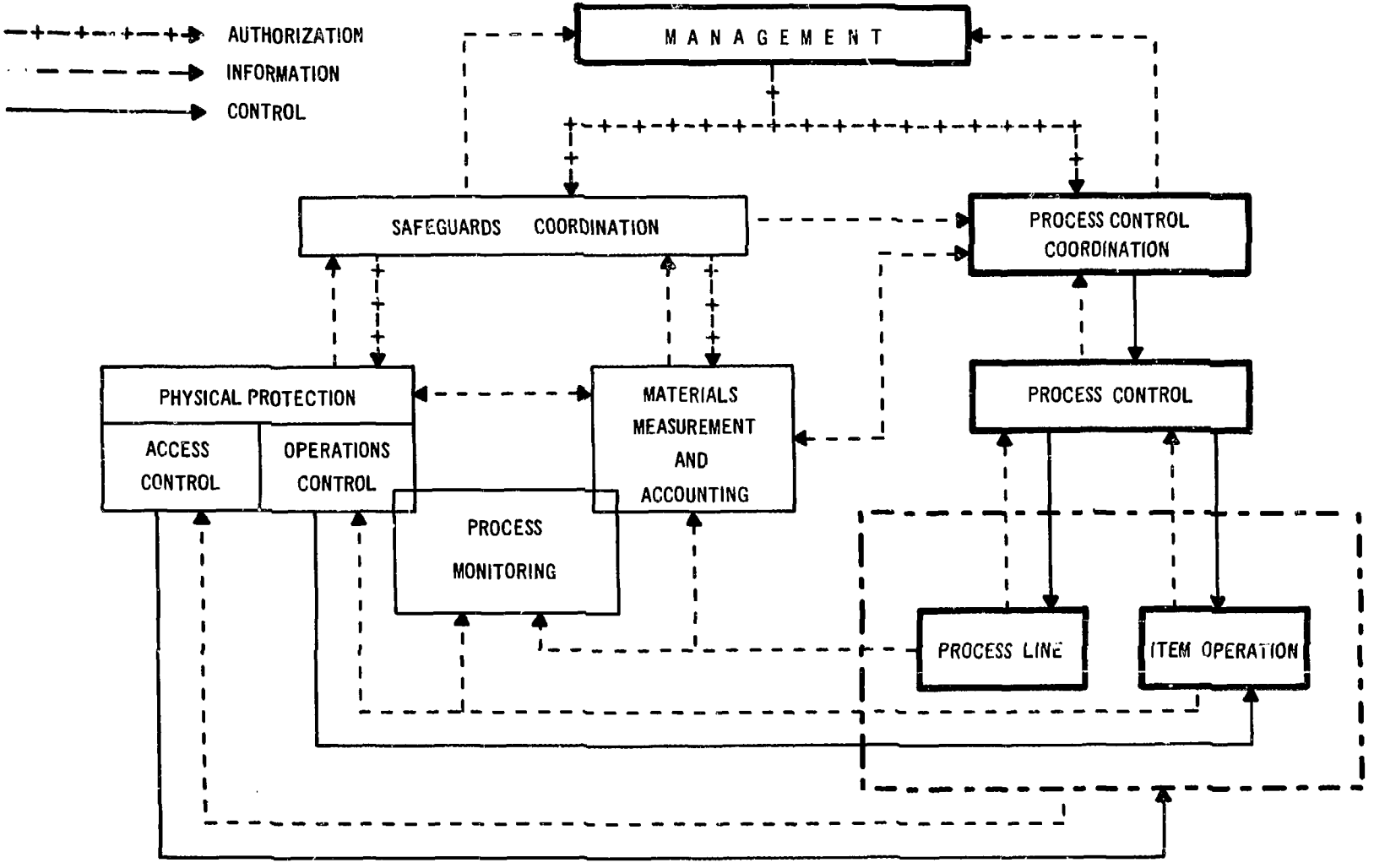


Fig. 11. Structure of the safeguards system.

must be balanced to avoid frequent false alarms that cause unnecessary process disruptions, while maintaining a high probability of effective response to any credible safeguards violation.

The SCU would normally rely on automated decision and control augmented by human supervision in abnormal situations. Although it is the heart of the safeguards system, the SCU must be carefully designed to minimize single-point vulnerability and to reduce the time necessary to respond to rapidly developing threats.

During normal process operation and when the safeguards status of the facility is satisfactory, the safeguards system performs primarily a monitoring function. Except for access control and some item operations discussed below, the safeguards system normally has very little impact on process operations. However, if a safeguards-related abnormality occurs, the SCU can make recommendations to the PCCU aimed at enhancing the safeguardability of the nuclear material. The weight carried by the SCU recommendation depends on the nature and severity of the abnormality; as many such situations as can be reasonably foreseen should be detailed in a manual of standard operating procedures.

The physical protection system (PPS) controls personnel entry and exit for the facility and for restricted areas inside. The system includes automated equipment and enough guard forces to provide effective response in an emergency. It expands the conventional security functions, such as personnel control, to include control of item-handling operations. This arrangement provides more effective protection through remote, overriding control of discrete material items in handling and storage. The concept is applied only to those portions of the facility, such as the loadout area, that are outside the closely coupled process line where materials flow is not critical to smooth process operations.

The PPS provides appropriate information to the safeguards system and

- excludes all unauthorized persons and contraband from the facility,
- admits only essential persons to selected areas, and
- precludes unauthorized activities involving nuclear material and vital equipment.

Important objectives in the design of the PPS are to automate its functions whenever possible and to harden the system against subversion. These objectives are consistent with the stated goal of reducing dependence on personnel reliability.

In the current concept of domestic safeguards, the physical-protection and materials-accounting functions complement and reinforce each other. In particular, the PPS protects not just nuclear material, but the integrity of the MMAS as well. Conversely, the MMAS confirms the effectiveness of the PPS. This approach requires a high level of technological sophistication in the system design and operation, supplemented by thorough and frequent plant and safeguards inspections by a knowledgeable, independent safeguards staff.

The design and evaluation of the PPS for these facilities is the responsibility of Sandia Laboratories. This is discussed in detail in Refs. 28, 29, and 33.

The MMAS is an implementation of the DYMAC concept,[35,36] and is similar in principle to that already described for several types of facilities. It combines conventional chemical analysis, weighing, and volume measurements with the near-real-time measurement and surveillance capabilities provided by NDA instrumentation to enhance rapid and accurate assessment of the location and amount of SNM in a facility. The concept of graded safeguards is employed to provide best measurement quality at the product end of the process where SNM is most attractive to a divertor.

The process-monitoring function combines elements of both the PPS and MMAS and provides supplementary information to each regarding compliance of actual process-operating modes with

approved procedures. The concept may be regarded as an extension of physical-protection monitoring and surveillance functions into the process line, and as an upgrading of the monitoring devices (or appropriate placement of them) to allow gross materials accounting.

The process-monitoring system collects timely information to detect a theft in progress from a limited set of on-line measurement equipment, plant-grade instrumentation, and other simple, reliable process-monitoring devices. The system uses plant instrumentation wherever possible to assess approximate material balances on transfers between tanks and across columns. Similarly, an overall plutonium balance can be maintained. This balance is crude by accounting standards, but has the advantage of near-real-time availability.

The system also uses an array of sensors to provide information on the status of process valves; presence or absence of liquid in process, sampler, and decontamination lines; status of valves supplying sample or transfer jets; and pressures in instrument lines. These sensors are all simple, rugged, and relatively inexpensive. This report will not discuss the physical protection and process-monitoring systems beyond the brief functional descriptions given.

The safeguards computer system plays an essential role in implementing effective safeguards by collecting safeguards-related data and maintaining and controlling the safeguards information system. A major part of this role is the protection of SNM; an equally important part is the operational effect of the computer system on the processing of nuclear material. This occurs because information provided through the computer system forms the basis for all safeguards decisions, which may have varying degrees of effect on the process. Erroneous or unavailable information can degrade decision quality and cause unnecessary process disruptions. Thus, the reliability and integrity of the computer sytem directly affect economical operation of the process.

Several of the many possible computer and information system implementations are discussed in Refs. 28 and 30. In addition, the TRW Defense and Space Systems Group, under subcontract to Sandia Laboratories, is now investigating this area and refining alternatives. References 37 and 38 present some of their preliminary results and discuss system security and reliability. Reference 39 presents availability analyses for several alternative high-reliability computer systems.

Analysis of materials-accounting data for possible SNM diversion is one of the major functions of the MMAS. The use of unit-process accounting and dynamic material balances enhances the ability to detect such diversions, but it also means that the operator of the safeguards system will be inundated with materials accounting data. Furthermore, although these data contain much potentially useful information concerning both safeguards and process control, the significance of any isolated (set of) measurements is seldom readily apparent and may change from day to day, depending on plant operating conditions. Thus, the safeguards system operator is presented with an overwhelmingly complex body of information from which he must repeatedly determine the safeguards status of the plant. Clearly, it is imperative that he be assisted by a coherent, logical framework of tools that address these problems.

Decision analysis (see Refs. 31, 40-43), which combines techniques from estimation theory, decision theory, and systems analysis, is such a framework, and is well suited for statistical treatment of the imperfect dynamic material-balance data that become available sequentially in time. Its primary goals are (1) detection of the event(s) that SNM has been diverted, (2 estimation of the amount(s) diverted, and (3) determination of the significance of the estimates.

Decision analysis based on mathematically derived decision functions is appealing because it can quantify intuitive feelings and condense large collections of data to a smaller set of more

easily understood descriptors (statistics). It can also eliminate personal biases and other errors caused by subjective evaluation of data while providing a degree of consistency for the decision process.

The safeguards system structure discussed above incorporates the latest safeguards concepts as determined by extensive interactions with the nuclear industry and workers in the safeguards field. These concepts provide not only guidance in developing new systems, but also a means of assessing the effectiveness of existing systems. The ideas are general enough to apply to any of the proposed alternative fuel cycles with only changes in detail.

The safeguards system can be implemented in many different ways using various levels of hardware sophistication. These range from completely automated, computerized systems to those that rely extensively on the human element. The optimum configuration is likely a mix of the two extremes, one that synergistically provides the best features of both.

B. Concepts for Thorium-Based Fuel Reprocessing

The materials flow for the thorium-based nuclear fuel plant was described in Chap. III, and the safeguards system structure was discussed in the previous section. The measurement methodology pertinent to materials accountability is reviewed in Chap. V.

The materials-measurement philosophy will be based on dividing the plant into as many individual materials-measurement areas as is practical from process-control and measurement considerations. Possible materials-measurement areas for the thorium-based fuel reprocessing plant are shown schematically in Fig. 12.

1. Fuel Receiving and Storage. The fuel receiving and storage area is a separate materials-control area (MCA). Accountability is by item control. The serial number of each fuel assembly is identified visually and is checked against the

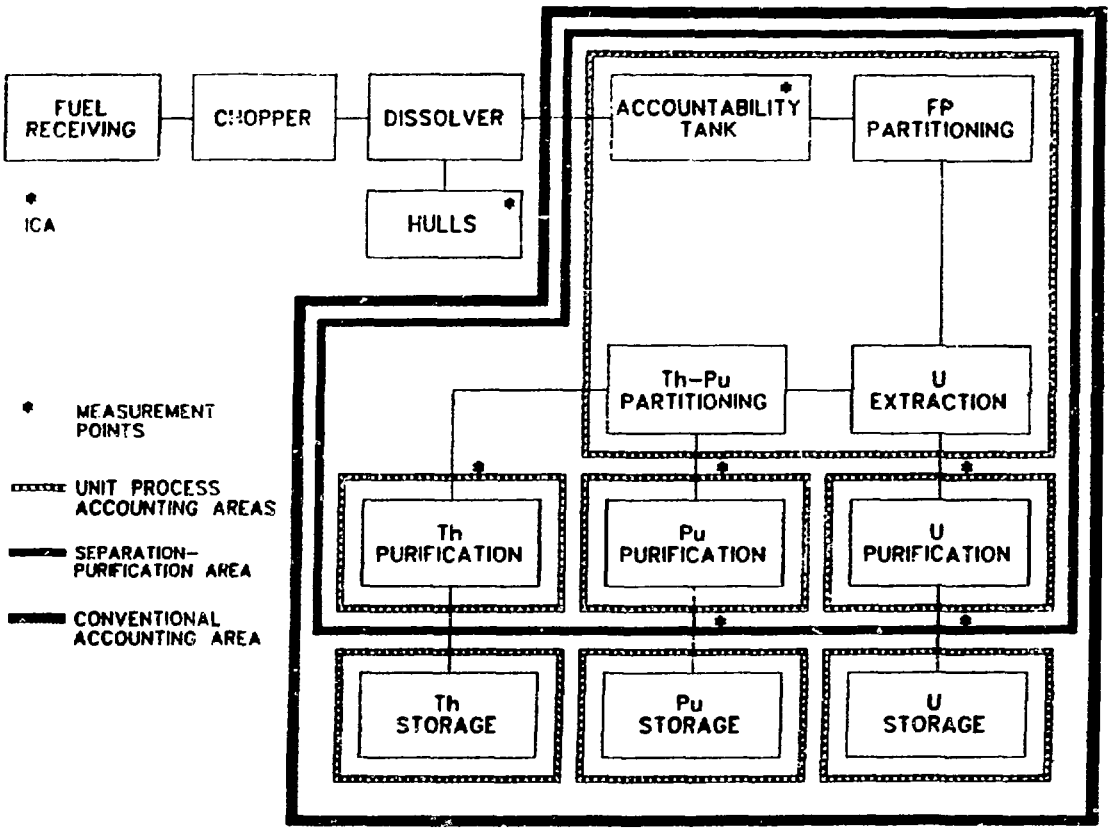


Fig. 12. Proposed unit process boundaries and measurement points for thorium fuel reprocessing plant.

accompanying shipping papers. The assemblies are stored in the storage pool while awaiting transfer to the shear. Gamma-scanning techniques may be applicable to verifying the existence of spent fuel in fuel bundles or rods. Gamma or neutron methods may be applicable to quantitative measurement of fissile content of spent fuel in storage pools.

2. Fuel Chopping and Dissolution. The fuel chopping and dissolution are performed batchwise on bundles of fuel elements transferred from the fuel storage pool, with 1 MTHM of fuel per dissolver batch. The fuel is chopped into segments 2.5-13 cm in length, and the pieces are diverted to a dissolver basket.

a. Leached Hulls. If fuel bundles are comparable to normal LWR fuel, each batch will yield approximately 290-390 kg of leached hulls per MTHM. (Ref. 20, p. 4-29). The hulls consist primarily of Zircaloy fuel-element cladding and stainless steel end fittings, but may contain undissolved fuel or fuel that has reacted with the Zircaloy to form compounds insoluble in the HNO_3-HF dissolver acid. Undissolved fuel may result from crimping of individual fuel pieces or inadequate dissolution conditions. In any event, hulls must be monitored for process control and safeguards considerations to assure that excess fuel is not diverted to waste, and to measure the amount of fuel lost.

Either neutron or gamma-ray methods may be used to measure fissile content of the hulls. A neutron method based on spontaneous fission and (α,n) neutrons yields a sensitivity of 2 mg of plutonium for a 10^4-s measurement time.[44] Because the spontaneous fission yield from uranium is significantly lower than from plutonium, uranium sensitivity is expected to be significantly lower (see Table III).

An indirect method based on measurement of the 2.1-MeV gamma ray of ^{144}Pr has been proposed (Ref. 20, p. 4-31; Ref. 45). The sensitivity of the technique is a function of fuel element age due to the 284-day half-life of the ^{144}Pr precursor, ^{144}Ce, and the method is not applicable for long-cooled fuels.

b. Dissolver Solution. It is probably not practical to obtain an accountability measurement directly in the dissolver.

3. Fuel Reprocessing. The fuel reprocessing area from the accountability tank through the thorium, uranium, and plutonium product storage tanks can be treated as one large materials-measurement area, or it can be subdivided into several smaller areas (refer to Fig. 12). Each of the three product-purification areas can be treated as separate measurement areas, with the portion from the accountability tank through the partitioning columns as a fourth measurement area. In order to better isolate diversion detection and to reduce measurement uncertainties, the multiple unit process approach will be considered.

a. Accountability Tank Through Partitioning. The accountability tank measurement is a key point, regardless of the measurement strategy. The measurement is obtained by a combination of bulk volume and concentration. Volume measurement may be either with a high-precision manometer after volumetric tank calibration or with load cells. The load cells theoretically could provide higher accuracy, but isolation of the tank from associated piping is required to eliminate damping and loading effects.

Accountability-tank concentration measurements for thorium, uranium, and plutonium can be made using isotope-dilution mass spectrometry, or possibly x-ray fluorescence.[46]

The outputs of the uranium partitioning and thorium-plutonium partitioning product streams may be measured at-line using absorption-edge densitometry. It may be necessary to incorporate an energy filter to minimize effects of fission-product and decay-daughter radiation.[47] Alternatively, at-line x-ray fluorescence could be used for all three product streams.

b. Uranium Purification. The input measurement to the uranium purification will be the same as the output from the uranium extraction cell. The output from the uranium purification area will be made after the product concentrator. Absorption-edge densitometry using the K-edge may be applicable.

Recycle waste streams from the uranium purification area to the partitioning area must be monitored. Uranium may be measured using at-line polarography. Plutonium may be measured using in-line alpha monitors.

c. Plutonium Purification. The safeguards accountability system for the plutonium purification area is anticipated to be similar to the system described previously for a uranium-plutonium fuel reprocessing plant.[31]

d. Thorium Purification. The input to the thorium purification area will be the same as the output from the

thorium-plutonium partitioning cell, and may be measured using at-line x-ray fluorescence or absorption-edge densitometry. The output from the thorium concentrator may be measured using absorption-edge densitometry or, possibly, gross density with an acid and temperature correction.

Waste streams recycled to the partitioning columns can be monitored for uranium using at-line polarography and for plutonium using in-line alpha monitors.

4. Product-Storage Areas. Product-storage tanks can be monitored by concentration and volume, using a dip tube manometer. Off-specification materials recycled through the purification system must be measured using concentration and volume based on batch transfers.

5. Liquid-Waste Tanks. Low-level liquid wastes are accumulated on a batch basis, analyzed for total uranium, plutonium, and thorium and concentrated for transfer to high-level liquid wastes.

Intermediate-level liquid wastes, basically originating from solvent purification systems, are accumulated on a batch basis, analyzed for SNM, and transferred to the intermediate-level liquid waste tank.

High-level liquid wastes, orginating from fission product partitioning, low-level liquid waste concentrates, and centrifuge sludge, are accumulated on a batch basis, analyzed for SNM, and transferred to the high-level liquid wastes.

6. Solid Wastes. In addition to the leached hulls described previously, miscellaneous solid process waste is accumulated throughout the process area. The waste is packaged in 55-gallon drums. Accountability measurement methods based on neutron or gamma-ray techniques must be developed and evaluated for measuring SNM in these drums.

V. MEASUREMENT METHODOLOGY

Both conventional chemical and nondestructive analysis techniques will be required to implement a near-real-time measurement control and SNM accountability system for a thorium-based fuel reprocessing plant. Any analysis scheme must consider such factors as standards, sampling, time of analysis, and applicability to the measurement requirements. The subjects of conventional and nondestructive analysis (NDA) techniques for safeguarding the uranium fuel cycle have been extensively treated in previous Los Alamos Scientific Laboratory (LASL) reports.[30-32] A critical review of analytical techniques for safeguarding the thorium fuel cycle will be released concurrent with this report as LA-7372;[48] a report emphasizing NDA techniques useful in safeguarding the thorium fuel cycle is forthcoming.

A. Standards

All procedures and instruments used for nuclear safeguards accounting should be calibrated against approved standard reference materials. All weight and volume measurements should be traceable to National Bureau of Standards (NBS)-certified weight standards. Class S weights certified by the NBS are used as reference standards for laboratory measurements. Volumes are calibrated using appropriate NBS-certified weights as reference standards.

The following primary standards are available for use as oxidation-reduction standards in the nuclear safeguards accountability program:

- SRM 136c - potassium dichromate
- SRM 83c - arsenic trioxide, and
- SRM 40b - sodium oxalate.

SRMs available for uranium and plutonium analyses are shown in Ref. 49, p. 42. The uranium isotopic standards are well suited for the analysis of uranium-thorium fissile fuels. However, secondary standards must be prepared for fertile fuels because primary standards containing ^{233}U are not available. In addition

to the NBS standards, standards for the spectrographic determination of impurities in uranium are obtainable from the New Brunswick Laboratory and the Oak Ridge National Laboratory.[50] Thorium primary standards presently are not available through the NBS. However, reference materials can be obtained from the New Brunswick Laboratory, and the NBS has initiated a program to develop a thorium standard reference material (SRM).

Secondary or bench standards may be working standards obtained from a source such as NBS, from various DOE contractors, or from international sources.[51] Alternatively, they may be prepared from process solutions by characterization against NBS SRMs. The preparation and evaluation of secondary plutonium-nitrate standards have been described[52] and should be incorporated into the analytical laboratory standard operating procedure. The same techniques are applicable to preparation of uranium working standards from plant uranium materials. These standards should be analyzed daily or by each shift to ensure that the method is under control. Process samples should not be analyzed until satisfactory values are obtained on bench standards.

Primary standards for chemical analysis also can be used for NDA applications, but generally must be incorporated into a matrix to simulate process samples. This can introduce errors, and these secondary standards must be evaluated for homogeneity, etc. The New Brunswick Laboratory has initiated a program to develop low- and medium-density NDA standards for uranium analyses.[53] The same technique can be used for plutonium and thorium reference materials.

B. Sampling and Sample Preparation

Measurements of process product and waste streams will require analyzing solids as well as solutions and, in some cases, heterogenous mixtures. Because of the high radiation levels associated with most process materials, remote sampling techniques will be required. The critical analytical points will be the accountability and product-storage tanks. The waste streams

will be of lesser importance but must be monitored, not only to measure the amounts of thorium, uranium, and plutonium going to waste, but to ensure that uranium and plutonium are not returned to process vessels for subsequent diversion and waste discard values overstated to conceal this action.

The air-lift sampling system should be designed to allow for extensive recirculation of solutions through the sample lines and the sample bottle during the sampling operation. Vessel sparging, mixing time, and sample-circulation time should be considered in establishing proper sampling procedures for replicate samples. Any solids must be dissolved after sampling and included in the total analysis. For highly radioactive samples the possibility of bubble formation must be considered in volume measurements, and temperature corrections should be applied.

The main sources of sampling error for solutions are expected to be (1) concentration or dilution of the sample by the air-lift system, (2) incomplete mixing of the solution in the tank, (3) contamination of the sample in the sample lines, and (4) sample heterogeneity caused by suspended solids. Where analytical precision, expressed as relative standard deviation (RSD), of better than 0.5% is required, all sampling should be done on a weight basis rather than a volume basis. Remote volume samplers can seldom provide routine precision better than 0.5%, and even normal volumetric measurements generally are no better than 0.2% on a routine basis.

A sampling apparatus capable of providing pipetting accuracy of $\pm$ 0.1% under hot-cell conditions has been described.[53] All steps including pipette rinsing are performed remotely, and the Teflon piston surface does not touch the solution being pipetted.

C. Conventional Analytical Techniques[54]

A number of chemical methods have been applied to the measurement of thorium, uranium, and plutonium in a wide variety of reactor-related materials. The methods are capable of providing

precision better than 0.1% (1σ) with high accuracy. High sensitivity (less than 1 mg) can be attained. Methods have been developed and evaluated using natural thorium and uranium or weapons-grade plutonium, and should be re-evaluated for reprocessing-type materials.

Most analytical schemes for thorium, uranium, or plutonium will require some separations from each other or from fission products, by means of precipitation, solvent extraction, or ion exchange techniques. Most separation schemes for these elements take advantage of the multiplicity of valence states for plutonium and to a lesser extent, for uranium. Thorium can be separated from both uranium and plutonium by oxidizing the latter to UO_2^{2+} and PuO_2^{2+}. Plutonium can be reduced to Pu^{3+} or Pu^{4+} to effect separation from UO_2^{2+}.

With or without separation, a suitable method is selected for analysis. The method should provide precision, accuracy, sensitivity, and speed as required for safeguards and process control considerations. A combination of conventional analytical chemical and NDA methods may be used to satisfy these requirements.

1. Gravimetric Methods. Gravimetric methods rely on separating a compound of the element to be determined and igniting it to a constant-weight stoichiometric compound. The method is applicable only to relatively pure materials; impurities must be determined using spectrographic or other procedures and the final weight corrected by difference. Where clean separations from impurities can be obtained, precisions of better than 0.1% often can be realized. The method is applicable to purified thorium and uranium product streams. However, it is difficult to obtain a stoichiometric PuO_2 product for weighing and this fact plus the hygroscopic nature of PuO_2 makes gravimetry a less-than-ideal method for determining plutonium.

2. Spectrophotometric Methods. Spectrophotometric methods rely on the property of a compound in solution to absorb monochromatic light proportionally to concentration. The RSD attainable by direct spectrophotometry generally is 0.5% or greater and seldom is better than 0.2%. However, differential techniques can improve the method to provide an RSD of ~0.05%.

Spectrophotometric techniques are applicable to reprocessing samples, particularly to determinations of all three heavy elements in waste streams. A method using tetrapropyl ammonia has been automated for the sequential determination of uranium and plutonium.[55,56] A differential technique can be applied to measuring plutonium in product storage tanks with a precision of 0.05% (1σ).[57]

3. Electrometric Titrations. Amperometry, potentiometry, and coulometry have been applied to the determination of uranium and plutonium with RSDs better than 0.1%, and probably provide the most accurate and precise methods for determining these elements in high-purity materials. The attainment of similar precision with reprocessing samples must be demonstrated.

Because the only oxidation-reduction couple for thorium, Th^0 - Th^{4+}, has a potential above that for the water couple, electrometric titrations are unsuitable for measuring thorium.

4. Polarographic Methods. In-line or at-line polarography has been investigated for determining uranium in reprocessing samples. Conventional polarography using a dropping-mercury electrode (DME) is a diffusion-dependent process and is applicable only in quiescent systems. With suitable sampling, sparging, and cell-construction techniques the method has been applied to determining uranium in waste streams with an RSD of 10% (1σ).[58] The method is being investigated for determining uranium in acid[59] and organic[60] waste and recycle streams in Japan and in HTGR reprocessing waste streams in Germany.[61]

The method warrants consideration as an in-line or at-line method for waste-stream uranium analysis in the reference facility.

5. Complexometric Titrations. Complexometric titration, primarily using (ethylenedinitrilo)tetraacetic acid, is applicable to determining thorium and Pu^{3+} or Pu^{4+} with an RSD of 0.1% (1σ). Complexometric titration will be a primary method for determining thorium and is preferred over gravimetry because of time considerations.

6. Mass-Spectrometric Methods. In most existing Purex reprocessing plants thermal-ionization mass spectrometry is used to determine the amount of each isotope of uranium and plutonium, and subsequently the effective atomic weights for calculating the total uranium and plutonium from chemical analysis of samples from the accountability tanks. Isotope-dilution mass spectrometry can also be used to measure the plutonium and uranium concentrations in the tanks.

For determination of plutonium, either ^{242}Pu or ^{244}Pu can be used as the spike, with the latter preferred if available, because it is not produced in significant quantities in the reactor. Uranium-233 is used as the spike for analyzing conventional LWR fuels. For ^{233}U measurement ^{235}U rather than ^{233}U is proposed as the spike because ^{233}U is the major isotope to be measured. Thorium-230 has been proposed as the spike for thorium determination.

For determination of major isotopes, RSDs of 0.01-0.02% (1σ) can be attained. The precision for well-characterized materials such as NBS SRMs generally is significantly better than for process and product samples, probably reflecting problems in sampling and sample preparation. Overall precision for measuring dissolver samples has been in the range 0.3-1%, but may be improved to 0.1-0.2% with more stringent quality control.[62]

7. Alpha-Spectrometric Methods. Alpha spectrometry is an isotope- rather than element-specific analytical method, and is most suitable for determining ^{238}Pu. With appropriate sample preparation, it has been applied to measuring plutonium in process samples of known isotopic compositions with an RSD of 3-5% (1σ).[63] The technique is particularly well suited to measuring low plutonium concentrations in waste streams. In-line alpha monitors having α/β discrimination factors of 10^4 and providing linear response to plutonium concentrations in the range 10^{-4}-1 g/L have been described for reprocessing streams.[64,65]

Alpha spectrometry also can be used for uranium analysis, but low concentrations of plutonium can interfere seriously. The technique is not applicable to the determination of thorium.

8. Fluorimetric Methods. Fluorimetry has evolved as a standard method for determining small amounts (1-100 ng) of uranium. The RSD for measuring uranium in simulated reprocessing plant waste streams was reported to be 13%.[66] A number of elements including thorium can interfere by quenching the uranium fluorescence.[67] The method is not applicable for determining thorium or plutonium.

9. Specific-Ion Electrodes. Specific-ion-sensitive electrodes have been studied for several years both for process control and analytical end-point detection. The applications of ion-selective electrodes to on-line analysis has been reviewed.[68] Although electrodes generally are not specific for thorium, uranium, and plutonium because all three are expected to behave similarly in the tetravalent state, the technique has elicited some interest, particularly for the determination of uranium.

Several attempts have been made to form uranium-sensitive electrodes. An electrode based on embedding a uranyl complex of an organophosphoric acid in a polyvinyl chloride matrix was patented in 1975.[69] A number of organophosphorous complexes were subsequently studied for their possible application as uranium-ion sensors.[70] Several sensors showing near-Nernstian

response and linearity to uranium concentration in the range 10^{-1} to 10^{-4} M were identified. The optimum pH range was 2-3.5. The membranes are poisoned by Fe^{3+}. Solid state electrodes fabricated from uranium alloyed with titanium, molybdenum, or niobium were found to give a linear response proportional to uranium concentration, but sensitivity was poor.[71] Electrodes of UO_2, U_3Si_2, US_2, UC_2, and UP did not respond. Membrane electrodes also were studied but response to uranium concentration was low and erratic.

Additional work on uranium-sensitive electrodes may be warranted for on-line or at-line measurement of low concentrations of uranium.

Specific-ion electrodes are of little or no interest for measuring thorium or plutonium at this time.

10. X-Ray Fluorescence Techniques. Although x-ray fluorescence measurements of SNM solutions have enjoyed wide exposure in the literature, current safeguards applications are limited because of competition from other less complex and less matrix-dependent methods. Wavelengthand energy-dispersive systems have been developed for analysis of reprocessing samples.[72-76] Analyses can be performed in the presence of fission products, generally by limiting sample size, with RSDs of the order of 1-2% (1σ). The methods have been automated to facilitate rapid analysis of process samples without overexposure of personnel.

11. Density Methods. A density method has been described for measuring thorium and uranium in their respective product storage tanks at a thorium-uranium reprocessing facility.[77] Density, temperature, and acidity are monitored remotely, and concentrations are computer-calculated using linear regression techniques. The method is not element specific, and is of questionable value for nuclear safeguards applications.

D. Nondestructive Analysis Techniques

Nondestructive analysis (NDA) techniques generally rely on measurement of phenomena associated with nuclear properties of the element, and hence are generally isotope rather than element sensitive. These may include neutron emission, gamma-ray emission, and calorimetry. In addition, x-ray and gamma-ray absorptiometry, which rely on atomic, rather than nuclear, processes and hence are element sensitive, are used.

Most NDA techniques will be adversely affected to some degree by the high gamma background from the ^{232}U and ^{228}Th decay chains.

1. Neutron Methods. Both passive and active neutron methods can be used to measure fissionable isotopes of uranium and plutonium. In passive neutron techniques either spontaneous fission neutrons or neutrons produced by (α,n) reactions can be used. Active neutron methods rely on measurement of prompt or delayed neutrons after excitation by an external neutron source.

a. Spontaneous Fission. The spontaneous-fission neutron yields for the thorium, uranium, and plutonium isotopes are summarized in Table III (Ref. 78). The low spontaneous neutron fission yields from all but ^{232}U and the low and variable concentration of the latter preclude this technique as a method for measuring thorium and uranium. Using coincidence-counting techniques to discriminate spontaneous-fission neutrons from (α,n) neutrons, the method can be used to measure plutonium in waste materials[79].

b. (α,n) Reactions. The (α,n) neutrons result from reactions of alpha particles from the radioactive decay of uranium or plutonium with light elements in the matrix material. The neutron yield is a function of alpha-particle energy, the (α,n) cross sections of the matrix elements, and the matrix configuration. Furthermore, the alpha-particle intensity depends on the isotopic composition and is particularly sensitive to the

TABLE III

SPONTANEOUS FISSILE (S-F) OF FISSIONABLE ISOTOPES OF Th, U, AND Pu

Nuclide	S-F Half-Life, years[a]	Neutrons/ S-F[b]	S-F/g-s[a]
^{230}Th	$>1.5 \times 10^{20}$		$<3.8 \times 10^{-7}$
^{232}Th	$>10^{21}$		$<5.7 \times 10^{-8}$
^{232}U	8×10^{13}		0.71
^{233}U	1.25×10^{17}		4.56×10^{-4}
^{234}U	2×10^{16}	2	2.8×10^{-3}
^{235}U	1.9×10^{17}	2	2.96×10^{-4}
^{236}U	2×10^{16}	2	2.8×10^{-3}
^{238}U	7.19×10^{15}	1.95	7.73×10^{-3}
^{238}Pu	4.9×10^{10}	2.26	1.1×10^{3}
^{239}Pu	5.5×10^{15}	2.2	1.0×10^{-2}
^{240}Pu	1.17×10^{11}	2.17	4.71×10^{2}
^{241}Pu	5×10^{15} [b]	2.2	1.1×10^{-2} [b]
^{242}Pu	7.06×10^{10}	2.16	8×10^{2}

[a] Ref. 78.

[b] Ref. 79.

^{232}U and ^{238}Pu contents. The assay of ^{233}U by the (α,n) reaction is complicated further by the grow-in of alpha-emitting daughters of ^{232}U, which result in a $\sim$75% increase in alpha activity from initial cleanup to equilibrium. As a consequence, (α,n) neutrons ordinarily provide no quantitative signature for plutonium, and, in fact, they usually constitute a large background that must be eliminated from most measurements.

c. Active Neutron Interrogation. Active methods of neutron analysis generally use a ^{252}Cf source and coincidence counting of induced-fission neutrons. Using thermal neutrons, fission occurs primarily in the odd-numbered isotopes. The method has been used to measure ^{233}U and ^{235}U in scrap materials in a device referred to as the "shuffler".[80] The technique also could be applied to measurement of in-process holdup in areas such as pipes, filters, tanks, etc.

A method using a ^{252}Cf source and measuring thermal and epithermal neutrons has been described for measuring fissile material in operating pulsed columns.[81]

2. Gamma-Ray Emission. Gamma-ray emission techniques have been applied to measurements of the various uranium and plutonium isotopes, with the exception of ^{242}Pu, which does not emit useful gamma rays. However, a gamma spectrum from a sample of ten-year-old ^{233}U containing 250 ppm of ^{232}U failed to show peaks other than the ^{232}U daughters (Ref. 4, p. 36). It is doubtful if the method could be applied to the analysis of reprocessed uranium from thorium-based samples with any degree of sensitivity or reliability.

Gamma-ray spectroscopy can be used to measure the relative isotopic abundances of the plutonium isotopes (with the exception of ^{242}Pu) in plutonium product materials, and to measure total plutonium concentration. The relative isotopic ratios are required for interpretation of calorimetric measurements or of neutron coincidence measurements of spontaneous fission of ^{240}Pu and ^{242}Pu. Relative isotopic measurements generally are obtained by using gamma-ray energies in a narrow energy region to minimize self-absorption effects, and by applying peak-stripping and background-subtraction corrections with a computer. The relative precision of this measurement can be better than 0.5% (see Ref. 32, App. B). Total plutonium concentrations between 0.1 and 400 g/L can be determined in a 30-min counting period with an RSD better than 1% and an accuracy of 0.5% by measuring the ^{239}Pu isotope.[82]

The solid low-level waste from the reprocessing plant may be packaged in 55-gal drums for disposal, and should be analyzed for ^{233}U, ^{235}U, and plutonium. A drum scanner that uses a NaI detector to measure the 414-keV gamma ray from ^{239}Pu can detect as little as 1 g of ^{239}Pu in a 5-min scan.[83] The relative accuracy for measuring 10 g of ^{239}Pu can be as good as 10% in matrices of low atomic number and ranges to 50% in unknown matrices. Hence, the measurement accuracy will depend largely on the administrative control exercised in sorting waste. This instrument is in advanced development and requires only additional field testing and evaluation.

An indirect gamma-ray technique using the activity of the ^{208}Tl daughter of ^{232}U has been developed for measuring ^{233}U in process scrap.[84] The age of the waste, the $^{232}U/^{233}U$ ratio, and thorium content must be known. Counting geometry and matrix composition also can affect results.

3. Gamma-Ray Absorption. Active gamma-absorption methods have been proposed for plutonium solution assay. These methods depend on absorption of a monoenergetic gamma ray by the plutonium in the sample. Use of either ^{241}Am (60 keV)[85,86] or ^{57}Co (122 keV) (see Ref. 82, p. 18) has been proposed. An RSD and relative accuracy of 1% are obtainable, but any variations in matrix composition, including solvent, are measured as plutonium. Use of a dual-energy absorptiometer, where the second energy is ∿500 keV, can minimize solvent and light-element interferences.[87] However, any heavy-element contaminants such as uranium, neptunium, and americium will be measured with the plutonium, and even elements of medium atomic number such as iron will interfere.

The method also can be applied to the determination of thorium and uranium, but the same considerations for interference apply. The technique is of questionable value for safeguards applications.

4. X-Ray Absorption. Gross x-ray absorption using either polychromatic[88] or monochromatic[89] x-rays has been applied to the determination of heavy elements. The method suffers from lack of elemental specificity as do gamma-absorption methods, and any variation in impurity-element concentrations or matrix composition will be measured as changes in thorium, uranium, or plutonium.

5. X-Ray Absorption-Edge Densitometry. Absorption-edge densitometry[82] is an element-specific analytical method that can be applied in-line or at-line to most measurement situations that are amenable to gross-absorption techniques. With proper choice of cell path length and K- or L_{III}-absorption edges, plutonium (or uranium) concentrations between 5 and 500 g/L can be measured with a relative standard deviation of better than 1%.

Using the L_{III} edges, uranium[90] and plutonium[91] concentrations between 5 and 40 g/L were measured with RSDs (1σ) in the range between 0.34 and 1%. Using K-edge techniques, plutonium in the concentration range between 150 and 500 g/L was measured with RSDs (1σ) in the range 0.2-0.5% (Ref. 92).

With a continuum x-ray source uranium and thorium or uranium and plutonium solutions can be analyzed simultaneously with RSDs ranging from ∿5% to better than 1% (1σ), depending on concentration ranges and ratios.[93] The method is applicable to radioactive samples, and thus could be used as an in-line measurement technique in reprocessing lines.

Use of a curved-crystal spectrometer as an energy filter may enable measurements to be made of thorium and uranium in the high gamma-radiation fields associated with ^{232}U and ^{228}Th daughters.[47]

6. Calorimetry. Calorimetry[94,95] is a nondestructive-assay technique based on measuring heat generated generally by the radioactive decay of alpha-emitting isotopes. All but a negligible part of the decay energy is transformed into heat when the decay particles (alpha, beta, and low-energy gamma) are

absorbed by the sample and calorimeter walls. For plutonium samples most of the heat is generated by ^{238}Pu. For uranium, ^{232}U and its decay daughters are the main source of heat. Because of the variability in ^{232}U concentration through the reprocessing plant and because most reprocessing plant samples are liquids, it is doubtful whether calorimetry will have any safeguards applications in the thorium fuel cycle.

E. Flow Measurement

Flow measurement instruments[96] in nuclear fuel reprocessing plants are used principally for process control where high precision is not a major requirement. However, dynamic materials measurement systems for safeguards accountability dictate accurate and precise monitoring of materials flow as well as concentration.

The most accurate means of measuring flow within a reprocessing plant is to follow the progress of batch transfers. Batch volumes can be measured to high accuracies (+0.025 cm or 0.1% of scale, depending upon the system). Measurement of the rate of change in tank inventory can give a highly accurate indication of flow rate and is the best technique available. Where materials accounting is handled by batch accumulation and analysis, this method is the most convenient and accurate for handling the accountability. Continuous rather than batch transfer is used in the reprocessing area, and other means of flow measurement are required.

Fluid transfers in reprocessing facilities often are executed by airlifts to headpots, which provide gravity feed to the various columns. Flow rates are determined by the inherent properties of the flowing liquid, although some control is possible by varying the levels in the headpots or by throttling motive air flow to the lift. Correlations of the lift rate with air-injection flows can be used to monitor liquid transfers. Under controlled and well-established conditions such as exist within the reference plant, flow rates can be monitored to within

5-10%. A few headpots are equipped with orifice meters that should improve accuracy and precision to ∿1%.

Ejectors (jets) are frequently used for transfers, and are preferred to mechanical pumps because they have no moving parts and are essentially maintenance-free. Flow rates may be correlated or calibrated with motive fluid pressure, fluid properties, and system geometry. Ejectors are normally used only for transfers, and the correlation of flow with operating conditions is less accurate than with the air lift-headpot systems.

Magnetic flowmeters have been proposed for the EXXON fuel reprocessing plant.[97] They are capable of measuring flow rates to an accuracy of ∿1%. A disadvantage of the magnetic flowmeter is that it needs a conductive fluid for proper function and therefore cannot be used in organic streams or in aqueous streams having low salt content.

The ultrasonic flowmeter[98-100] is capable of measuring flow with an accuracy of better than 1%. Transducers can be mounted either in the pipe or exterior to the pipe wall so that intrusion into the pipe is not necessary. Pipe diameter is a limiting factor: diameters >4 cm (1.5 in.) are generally recommended. Interference by entrained air can be eliminated by transducer and detector-circuit design.[101] The use of ultrasonic flowmeters and extrinsic factors affecting measurement accuracy have been reviewed by Managan.[102]

A bubble flowmeter is under evaluation at the Idaho Falls Chemical Separations Plant for measurement of low flow rates, such as may be encountered in product concentrator lines.[103] This flowmeter measures the transit time of a small bubble injected into the flowing stream. Ultrasonic detectors mounted on the outside of the line detect the passage of the injected bubbles.

F. Volume Measurement

Volume determinations usually are inferred from the measured liquid level in a calibrated tank. At present, the best

developed liquid-level measuring system for use in nuclear facilities is the dip-tube manometer, or pneumatic bubbler. When combined with a commercially available electromanometer, such systems can have a detection sensitivity of 0.25 mm of water. Furthermore, the instrument output is directly computer-compatible. With careful calibration and an effective measurement-control program, calibration errors approaching 0.1% RSD and single volume-measurement errors of 0.5% or less should be attainable.[104]

G. Weighing Methods

Load-cell weighing systems are particularly well suited for measuring bulk quantities of material in nuclear reprocessing plants, and may be used for accountability and product tank measurements. The weighing platform can be separated physically from the associated electronics and readout mechanism. Only the platform need be exposed to the environment of a glovebox or process area, and the electronics can be located elsewhere to provide ready access for calibration and maintenance.

Load cells having 10-, 100-, and 1000-kg capacities are available commercially. These units have the following measurement errors (per cent of full scale) (see Ref. 30, p. C-23):

Zero balance	1%
Hysteresis	0.02-0.05%
Repeatability	0.01-0.03%
Linearity	0.05-0.25%

Determination by weighing the mass of solution in large process tanks and vessels would be the most direct method of obtaining this information, but successful use of load cells for such measurements has not yet been demonstrated. The Idaho Chemical Processing Plant has evaluated the in-plant performance of a load-cell weighing system on an existing input accountability tank.[105] Because of large thermal forces generated in the tank and attached piping, it was impossible to attain the

measurement accuracy for which the weighing system was designed. The study showed that to obtain useful accuracy, tanks installed on weighing systems must be specially designed for the application. Load cells also are being evaluated for the Japanese Tokai-Mura reprocessing plant.

VI. SUMMARY AND CONCLUSIONS

A preliminary conceptual design for a safeguards materials-management system for a 1500-MT/yr thorium-based nuclear fuel reprocessing plant has been proposed. The preliminary plant design is based on a combination of Purex and Thorex reprocessing technology to produce separate thorium, uranium, and plutonium product streams. No attempt is made to maintain the isotopic integrity of ^{233}U and ^{235}U reprocessing streams except by campaigning these fuels separately. The materials flows and reprocessing schemes are summarized in Chap. III.

The materials-measurement and accounting system combines recently developed NDA technology, state-of-the-art conventional measurement methods, special in-plant sensors, process instrumentation, and powerful data analysis techniques, supported by computer and data base management technology, and is described in Chap. IV. Various materials-measurement philosophies will be modeled to determine the most effective scheme for dividing the plant into materials balance areas (MBAs). The key measurement points are the accountability tank and the plutonium and uranium product storage tanks. Concentration-volume measurements in the accountability tank will be made by isotope-dilution mass spectrometry and dip-tube manometers. The product storage tanks will be monitored for concentration using conventional analytical chemical techniques, and for volume or mass using either dip-tube manometers or load cells. Additional MBAs may be drawn around the fission product decontamination-partitioning section and the three product purification areas using in-line NDA techniques combined with flow measurements. In-line or at-line measurements

for thorium, uranium, and plutonium separately or in binary or ternary combinations have been proposed using x-ray absorption-edge densitometry, alpha monitors, polarography, or x-ray fluorescence, supported by conventional analytical chemistry. The applicability of both conventional and NDA techniques to process streams that may contain significant background radiation from ^{232}U and ^{228}Th daughters must be demonstrated. Measurement technology as it may apply to the thorium fuels reprocessing plant is summarized in Chap. V.

The effectiveness of any particular measurement control strategy is a complicated function of many factors including operating procedures, management philosophy, and process constraints. For reliability and credibility, the evaluation and selection process requires computerized modeling and simulation methodology coupled with powerful decision analysis tools.[30-32,41-43] Our experience has shown that a specific facility must be modeled to maintain the necessary contact with reality; in this case, a final design to be selected by SRL will be the reference facility. Accountability measurement techniques (based on the best available estimates of performance and sensitivity) and the statistical sampling plans will be applied to the simulated SNM inventories. Alternative accounting and diversion strategies will be evaluated and compared using analysis tools adapted for this purpose. Recommendations made on the basis of these future comparisons will be presented in a subsequent final report.

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